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THE USE OF ELECTROLYTES IN THE PURIFICATION AND PREPARATION OF CLAYS

BY

H. G. SCHURECHT

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THE USE OF ELECTROLYTES IN THE PURIFICATION AND PREPARATION OF CLAYS.

By H. G. Schurecht.

INTRODUCTION.

As clays are of secondary origin, being derived from the decomposition and disintegration of the primary rocks, they differ in both physical and chemical constitution, depending upon the character of the original rocks and the conditions of deposition. Clays are not definite minerals, but they are made up largely of mineral fragments ranging in size from comparatively coarse grains to colloidal particles so fine that they can exhibit Brownian movements.

Clay can be obtained so finely divided that they can make true colloidal solutions. Colloidal clay belongs to the class known as "suspensoids" and is reversible—that is, the particles can be dispersed in water or thrown out of colloidal solution by means of suitable electrolytes. The action of electrolytes has been an extremely valuable aid both in the purification of clay and in the casting of clay wares. New applications are continually being discovered.

In one part of this paper the relation between the percentage of alkali necessary to maintain minimum viscosity in clay slips is studied with varying proportions of the slips. A knowledge of this relation is of fundamental importance not only in the purification of clays, but also in the casting of clay wares. The limits within which the slips can be successfully treated with electrolytes in the purification and casting processes are often relatively narrow, and any erroneous additions of electrolytes would cause serious trouble.

Statistics [1] show that the total clay or earths imported into the United States during the 12 months ending June, 1916, amounted to 228,235 tons, valued at $1,705,995. Compared with the 345,419 tons, valued at $2,246,807, that were imported into this country during the 12 months ending June, 1914, this figure shows a large decrease, due chiefly to the World War. Many manufacturers in this country have had to rely on domestic clays to take the place of those previously imported. Many domestic clays that are too impure to be used in the crude state can be utilized after purification. In order to improve the quality and uniformity of the product and to increase the output in purifying clays, it is necessary to maintain minimum viscosity in the clay slip during certain stages of the treatment. This minimum is governed by the quantity of alkalies added to the slip.

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[1] Monthly Summary of the Foreign Commerce of the United States: Bureau of Foreign and Domestic Commerce, June, 1916, p. 6.

The correct addition of alkalies to the casting slip is essential in the casting of clay wares. Heavy wares are not cast as extensively in this country as in Europe. For instance, the casting of glass pots and other refractories is being carried on with success in many places in Europe, but it is practiced only to a limited extent in this country, although it is claimed that the cast pots are of better quality, will last longer, and can be made at less cost than the handmade pots. On this point, however, there is much difference of opinion.

The use of sulphuric acid for neutralizing the sodium hydroxide, thus causing a sedimentation of the clay in the purification of kaolins with alkalies, has in some cases caused the kaolin refiners considerable trouble. The common troubles reported are the following:

1. In some cases the plasticity of the kaolin after it had been treated was much greater than the original plasticity.

2. A black scum appeared on the kaolin upon drying. As one of the commercial requirements of a paper clay is "white color," this defect would tend to render the kaolin unsuitable for the better grades of paper. The causes of these troubles were studied in order to outline the precautions necessary to overcome the troubles.

One of the sources of loss in the manufacture of clay products, especially heavy wares such as chemical stoneware and glass pots, by the plastic and casting processes is lack of strength of clays in the dry state and at the firing temperature. Strength enough to resist the shocks and strains of handling in the green or dry state is necessary. At certain periods during the burning in the kiln the ware loses strength and is liable to warp, crack, or break, causing heavy losses. The natural remedy would be to improve the strength of the clay body by artificial means or to introduce stronger clays.

In preliminary work it was found that a surprising increase in strength was gained by adding alkalies to clay in the plastic state. In some instances the strength of the treated clays was four times as great as that of the untreated. Part of the investigation was limited to a study of the effects of different additions of alkalies and acids on the properties of clays with special reference to their influence on the strength.

Many clays, which otherwise possess good properties, lack in plasticity and strength, and their use therefore is limited. In certain localities plastic clays of the fire-clay type are comparatively scarce, whereas the nonplastic fire clays are abundant. Part of the purpose of this work was to determine how much the plasticity and strength of nonplastic clays could be increased by special treatment such as wet grinding, adding electrolytes, removing the coarse material by screening, and adding an organic binder such as dextrine.

ACKNOWLEDGMENTS.

The writer wishes to acknowledge his indebtedness to R. T. Stull, Prof. A. S. Watts, and H. W. Douda for their assistance in this investigation. Mr. Stull gave helpful suggestions on the work and in the preparation of the manuscript. Prof. Watts suggested the work on the topic, "The relation of salt to clay in the purification of clays," and "The use of sulphuric acid in the sedimentation of clay." Mr. Douda assisted in the laboratory work on the section entitled, "The effect of wet grinding, screening, electrolytes, and dextrine, on clays of low plasticity and strength."

USE OF ELECTROLYTES IN PURIFYING CLAYS.

RATIO OF ELECTROLYTE TO CLAY OR WATER.

The effect of acids, alkalies, and salts on clay slips has been investigated by many persons, but little work has been done to show whether the ratio of electrolyte to clay in slips, or the concentration of electrolyte is the dominant factor in determining how much alkali should be added to slips differing in water and clay contents. Böttcher[2] determined the effect of alkalies on the viscosity of clay slips containing about 44 per cent clay and 56 per cent distilled water. He diluted portions of each slip thus treated until it contained about 4 per cent clay and 96 per cent water. His results show that the minimum viscosity in slips high in clay corresponds approximately to maximum deflocculation in the slips high in water. This fact would indicate that the ratio of electrolyte to clay is more important than the ratio of electrolyte to water in the slip, in determining how much alkali should be added, because changing the ratio of alkali to water and keeping constant the ratio of alkali to clay did not change much the point of maximum deflocculation. This result is in agreement with results obtained in the following investigation.

Ashley[3] using 0.1 molar sodium oxalate, the total volume always being 100 c. c. gives the following results:

Results of adding sodium oxalate.

Weight of clay.	Amount of reagent giving maximum suspension.	Amount of reagent per gram of clay.
Grams.	*c. c.*	*c. c.*
20	60	3.0
5	13	2.6
1	11	11.0
0.1	11	110.0

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[2] Böttcher, M., Ueber de Verflüssigung des Tones durch Alkali: Sprech., 1909, Jahrg. 42, p. 169.

[3] Ashley, H. E., Technical control of the colloidal matter of clays: Bureau of Standards Tech. Paper 23, 1913, pp. 45–46.

The figures indicate that in the high-clay slips the dominant factor is the ratio of electrolyte to clay, but in the high-water slips the ratio of electrolyte to water becomes important. The high-water slips here given, however, contain lower percentages of clay than those ordinarily used. The work presented in this paper deals only with slips containing more than 5 per cent clay.

According to T. G. McDougal,[4] "The curves which show that maximum thinning, indicating maximum conversion of gel. to sol. is effected by adding the same quantity of carbonate of soda per 500 c. c. regardless of the different amounts of clay in suspension, indicate that the effect produced is dependent upon the concentration of the carbonate in the water present. Curve 3 indicates a maximum point with somewhat lesser additions than in the case of curves 1 and 2, which can be explained by the fact that slip 3 contained more solid material and consequently less water (in 500 c. c. of slip) and, therefore, the concentration required for maximum effect was sooner reached."

It appears, therefore, that the data published by the different investigators are not consistent, some claiming that the electrolyte should be added in terms of water regardless of the amount of clay in the slip, and others claiming that sometimes the electrolyte should be added in terms of clay in the slip, regardless of the amount of water present.

FLOCCULATING EFFECT OF SULPHURIC ACID.

Probably one of the first persons to notice the flocculating effect of sulphates on clay was Forster,[5] who noticed that $CaSO_4$ dissolved from plaster molds retarded the deflocculating effect of sodium hydroxide. He therefore recommended the use of sodium carbonate instead of sodium hydroxide, thereby precipating the calcium as calcium carbonate and preventing the formation of calcium hydroxide.

Hirsch [6] found that soluble sulphates were not absorbed by the kaolin or the clay in the slip. According to Rieke,[7] in the case of iron and aluminum sulphates, the iron and aluminum are absorbed by the clay probably as hydroxide, and the sulphate radicle remains in solution.

Mellor, Green, and Baugh [8] found that calcium sulphate thickens a slip, and that potassium sulphate and potassium bisulphate first make a slip more fluid, then thicken it.

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[4] McDougal, T. G., The casting of clay wares: Tech. Paper 126, Bureau of Mines, 1916, p. 13.

[5] Foerster, F. Ueber das Gieszen des Tones: Chem. Ind. 1905, Jahrg. 28, pp. 733–740.

[6] Hirsch, H. Verhalten von Ton in Salzlösungen, Tonindustrie Ztg., Jahrg. 28, 1904, pp. 491–493.

[7] Rieke, R. Ueber die Wirkung löslicher Sulfate auf Kaoline und Tone: Sprech., Jahrg. 51, 1910, p. 757.

[8] Mellor, J. W., Green, S. A., and Baugh. Studies of clay slip. Trans. Eng. Ceram. Soc., vol. 6, 1906–7, pp. 161–170.

Rieke[9] says that magnesium sulphate, calcium sulphate, iron sulphate, zinc sulphate, copper sulphate, cobalt sulphate, and aluminum sulphate increase the viscosity of a Zettlitzer kaolin slip. Sodium and potassium sulphate increase the viscosity when added in small quantities but larger additions decrease it.

EFFECT OF ORGANIC BODIES.

The effect of the addition of organic compounds when added to plastic bodies has been studied by Acheson,[10] Minton,[11] Seger and Kramer,[12] and Koerner.[13]

It has been shown that the strength of the clays can be increased by adding gallo-tannic acid, catechu, straw emulsion, dextrine, or starch.

EFFECT OF ELECTROLYTES ON VOLUME SHRINKAGE.

The effect of the additions of alkalies and acids on the volume shrinkage of clays in the plastic state has been reported by Bleininger and Fulton,[14] and Kerr and Fulton,[15] but our information as to the effect of these electrolytes on the strength of clays is meager. Bleininger[16] has reported that cast bodies containing alkalies may be stronger than bodies not containing alkalies.

Staley[17] found that the addition of alkalies increased the tendency of clays to crack. He worked with a poor grade of clays, however, which have a tendency to crack in drying, and, furthermore, the test pieces used by him contained 100 per cent clay. A large number of bodies present no serious drying difficulties but still are weak; these would be benefited by the use of alkalies to strengthen the body.

CLAY WASHING.

TUBS AND CYLINDERS.

In the United States clays are usually washed by one of two methods. In the first, the clay is placed in large tubs filled with water and is disintegrated by revolving arms. This method removes most of the coarse material like sand and coarse grains of mica, kaolinite, feldspar, and quartz. The clay with the fine grains of mica, feldspar, and quartz remains in suspension and is drawn off into settling tanks.

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[9] Rieke, R. Work cited, p. 757.

[10] Acheson, E. G. Egyptianized clay. Trans. Amer. Ceram. Soc., vol. 6, 1904, pp. 31-64.

[11] Minton, R. H. An investigation of the E. G. Acheson process of toughening clays. Trans. Amer. Ceram. Soc., vol. 6, 1904, pp. 231-259.

[12] Rohland, Dr. P. Die Tone, Vienna and Leipzig, 1909, p. 82.

[13] Rohland, Dr. P. Work cited, pp. 82-84.

[14] Bleininger, A. V., and Fulton, C. E. The effect of acids and alkalies upon clay in the plastic state. Trans. Amer. Ceram. Soc., vol. 14, 1912, pp. 827-839.

[15] Kerr, C. H., and Fulton, C. E. The effect of some electrolytes on typical clays. Trans. Amer. Ceram. Soc., vol. 15, 1913, pp. 184-192.

[16] Bleininger, A. V. Use of sodium salts in the purification of clays and in the casting process: Bureau of Standards Tech. Paper 51, 1915, p. 40.

[17] Staley, H. F. The effect of the addition of salts on the drying properties of clays. Trans. Amer. Ceram. Soc., vol. 17, 1915, pp. 697-711.

Another method similar to this consists in using a large cylinder, closed at both ends, which is set in a horizontal position. Iron arms rotating about a horizontal axis break up the clay lumps and the fine particles of clay are carried off by a current of water, while the coarse material remains in the cylinder. The speed of the current must be so regulated that it removes only the fine material, and at the same time it should not be too slow. This method is not continuous, for stops are necessary from time to time in order to remove the coarse sand from the cylinder.

WASHERS AND TROUGHS.

The second method [18] is in more general use. It consists in first putting the clay in a clay washer, a rectangular box in which arms rotating about a horizontal axis help to disintegrate the clay. It is common practice to use two washers, allowing the material to pass from the first washer into the second. When sodium salts are used to deflocculate the clay they are usually introduced in the second washer. From the washers the clay passes to the sand wheels, which consist of wheels bearing iron scoops and revolving in narrow tanks, the sand being scooped from the bottom of the tank and thrown outside. Two sand wheels are generally used, the clay then passing to a series of troughs.

The sand trough is about 20 to 30 feet long, about 2 feet wide, and is placed absolutely level. A barrier 4 to 8 inches high is put at the outlet to assist in decreasing the flow, thus allowing the coarse sand to settle and preventing it from getting into the mica troughs. This sand is removed with a shovel by a workman. The square tank sometimes used in place of the sand trough is 6 feet long, 5 feet wide, and 1 foot deep. The outlet is placed either at right angles to the intake or at the same end as the intake. The sand deposited is removed by shovel.

The clay now passes into mica troughs that remove the mica and the finer impurities. These troughs are U-shaped, usually 1 foot wide and 1 foot deep, the total length being about 700 feet. In order to reduce the area needed, the troughs are broken into lengths about 40 to 50 feet, which are arranged parallel, and the slip passes through in a zigzag course. The flow is regulated by either a pitch of 1 inch between end and end or by building the troughs level with a drop

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[18] For fuller details see Watts, A. S., Mining and treatment of feldspar and kaolin: Bull. 53, Bureau of Mines, 1913, pp. 72–78. Ries, H., Clays of Maryland, Maryland Geol. Survey, 1902, pp. 271–276. Sproat, I. E., Kaolin refining: Trans. Amer. Ceram. Soc., vol. 18, 1916, pp. 767–811.

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of 1 inch between them. The impurities deposited are removed every 5 hours; during the removal the washing necessarily stops. If the sediment is not removed the channel becomes narrow, thereby increasing the rate of flow of the slip, carrying the coarser material farther along and making the product less uniform. When sulphuric acid is added the slip is run through a long narrow trough 1 foot wide, 1 foot deep, and 50 feet long. This trough allows the sulphuric acid to become mixed thoroughly with the clay slip.

The slip next passes through the screens which are covered with a copper screen cloth. An excess of sulphuric acid should be avoided, as it attacks the screen and reduces its life. The stationary screen, which is commonly used, consists of two or three wooden frames (about 4 inches high) covered with copper cloth and arranged so that the upper screens overlap the lower. The material that overflows from the upper screen flows into the lower screens through openings 2 inches wide across the lower end of the upper screen. The revolving screen is a cylinder covered with a fine wire screen and tilted at a slight angle from the horizontal. The slip fed in at the upper end is separated from the coarse material, which slowly works toward the outlet at the lower end.

The fine material that goes through the screen passes into settling tanks in which the slip stands until the clay has settled enough to remove the excess of water. The excess water is removed and the slip is then passed into an agitator, similar to a plunger. The slip, kept homogeneous by the revolving paddle of the agitator, is dewatered by pumping it through filter presses. The clay cakes are removed from the filter press and dried by open-air driers, steam driers, or tunnel driers.

EFFECT OF CONCENTRATION OF ELECTROLYTES ON THEIR CHEMICAL ACTIVITY.

The chemical activity of electrolytes varies with electrical conductivity. Table 1 gives the molecular conductivities of some electrolytes in different concentrations of water and shows how the chemical activity is increased by dilution in water.

In the purification of clays and the casting of ceramic wares, the normal concentration of electrolyte in water necessary to produce maximum effect varies between 0.025 and 0.001. Within these limits (see Table 1) the changes in conductivity for "strong" bases and acids such as are commonly used in ceramics, are relatively small, but those for "weak" reagents are relatively large. In studying the effects of adding electrolytes to plastic bodies, the concentration necessary to produce maximum effect is between 0.75 and 1.5. The chemical activity varies considerably between 0.001 and 1.5 concentrations; thus to produce the same effect more electrolyte in terms of clay is added when working with 1.5 concentration than when working with 0.001 concentration.

TABLE 1.—*Molecular conductivity at 18° C.*[a]

Normal concentration.	NaOH.	KOH 1/2.	Na_2CO_3.	NH_4OH.	1/2 H_2SO_4.	HCL.	HNO_3.
0.0001..	....	....	....	66	....	....	....
.0002..	....	....	....	53	....	....	....
.0005..	....	....	....	38	368	....	....
.001...	208	234	112.0	28.0	361	377	375
.002...	206	233	108.5	20.6	351	376	374
.005...	203	230	102.5	13.2	330	373	371
.01....	200	228	96.2	9.6	308	370	368
.02....	197	225	89.5	7.1	286	367	364
.05....	190	219	80.3	4.6	253	360	357
.1.....	183	213	72.9	3.3	225	351	350
.2.....	178	206	65.9	2.3	214	342	340
.5.....	172	197	54.5	1.35	205	327	324
1.......	160	184	45.5	.89	198	301	310
2.......	131.4	160.8	34.5	.532	183	254	258

[a] This table of Kohlrausch and Holborn was taken from Senter, G., Outlines of Physical Chemistry, 1916, p. 420.

EFFECT OF ELECTROLYTES ON CLAYS.

The addition of certain alkaline salts to clay slips in small quantities liquefies the slips, and the fine clay particles remain in suspension, while the coarser particles settle to the bottom. The separation of coarser material from the fine clay also takes place to some extent when no alkalies are used, but a large percentage of fine clay is carried down mechanically with the coarser particles. Using alkalies in the purification of clays makes possible a sharper separation between the coarse impurities and the fine clay.

Forster[19] claims that this action of electrolytes on clays occurs because the negatively charged OH ions repel the similarly charged clay particles, causing a liquefaction of the clay slip. Spangenberg[20] claims that the OH ion is adsorbed by the clay particles, and the particles so charged repel each other, thus causing the clay slip to become more liquid. When more than a certain amount of the electrolyte is added, the slip thickens. Acids and most acid salts cause a thickening or flocculation of clay slips.

When a slip that has been treated with alkalies is allowed to stand, it gradually thickens. Neubert[21] showed that slips containing alkali concentrations less than the degree required for maximum fluidity, thicken when allowed to stand, but slips containing more alkali than that amount become more fluid on standing. Other factors, like temperature, humidity, and degree of blunging, also affect the viscosity of clay slips.

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[19] Foerster, F., Ueber das Giessen des Tones: Chem. Ind., Jahrg. 28, 1905, p. 551.

[20] Spangenberg, A., Zur Erkenntnis des Tongiessens, ihren Einfluss auf die Tonverflussigung, 1910. Neubert, J. K., Die Tonverflussigung durch Alkali: Sprech., Jahrg. 46, 1913, p. 524.

[21] Neubert, J. K. Work cited, p. 568.

RELATION OF SALT TO CLAY IN THE PURIFICATION OF CLAYS.

DESCRIPTION OF TESTS.

To study the relation between the concentration of electrolytes necessary to produce minimum viscosity in clay slips and the concentration of clay in the same, the salt, clay, and water contents were varied by means of triaxial diagrams, and viscosity measurements were made with a viscosimeter similar to the one used by Bleininger.[22] The clay after being screened through a 120-mesh sieve was dried at 110° C. for 48 hours previous to the testing. Distilled water was used in all of the work, and the slips were allowed to stand 1 hour after being made up and then were tested. The temperature of the slips was kept within 5 degrees of 18° C.

The time necessary for 250 c. c. of slip to pass through an orifice of $\frac{3}{32}$ inch was measured with a stop watch. In the high-water slips checks were made by passing the slip through an orifice of $\frac{1}{32}$ inch. The time necessary for the same amount of water at 18° C. was then measured. The densities of the slip and water were determined, and by means of the following equation the relative viscosities, x, were calculated:

$$x=\frac{dt}{d_w-t_w}$$

In this equation, which is used for calculating relative viscosities for liquids with the Ostwald viscosimeter,[23] d and d_w are the densities of the liquid and water, respectively, and t and t_w are times required for the discharge of equal volumes of liquid and water, respectively. Owing to the fact that a clay slip is not a true liquid and owing to the difference in the construction of the viscosimeters, this equation is not exactly correct under the experimental conditions; for this investigation, however, it is accurate enough for practical purposes.

MATERIALS USED.

The clays studied were (1) a kaolin from Gordon, Ga., and (2) a ball clay from Mayfield, Ky., whose chemical analyses are as follows:

Analyses of clays used.

	1.	2.
Loss on ignition	13.62	11.52
SiO_2	44.25	46.87
Al_2O_3	38.06	36.58
Fe_2O_3	1.03	1.14
CaO	.08	.50
MgO	Trace.	Trace.
TiO_2	1.29	.43
Na_2O	.10	Trace.
K_2O	.70	1.60
S	.06	.06
Moisture loss at 105° C	.38	1.60
	99.58	100.30

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[22] Bleininger, A. V. Notes on casting: Trans. Amer. Ceram. Soc., vol. 17, 1915, p. 331.

[23] Senter, G. Outlines of physical chemistry, 1916, p. 75.

The electrolytes used were sodium hydroxide (NaOH), sodium silicate (Na_2O 3.1 SiO_2), and sodium carbonate (Na_2CO_3).

RESULTS OF TESTS IN PURIFICATION OF CLAY.

SODIUM HYDROXIDE AND GEORGIA KAOLIN.

Table 2 and figure 1 give the results of adding sodium hydroxide to Georgia kaolin. In figure 1 the isoviscosity lines show that the decrease in viscosity is retarded to a certain point, when the viscosity drops to a minimum and then with larger additions of alkalies viscosity gradually increases. The point of minimum viscosity is much better defined in high-clay slips than in low-clay slips, because the change in viscosity in the latter is very small. When sodium silicate or sodium carbonate is used (see figs. 2 and 3) the decrease in viscosity is not retarded as in using sodium hydroxide, probably on account of the presence of flocculating impurities,[24] like calcium hydroxide, that are precipitated on the addition of reagents like sodium carbonate, and are thus rendered harmless.

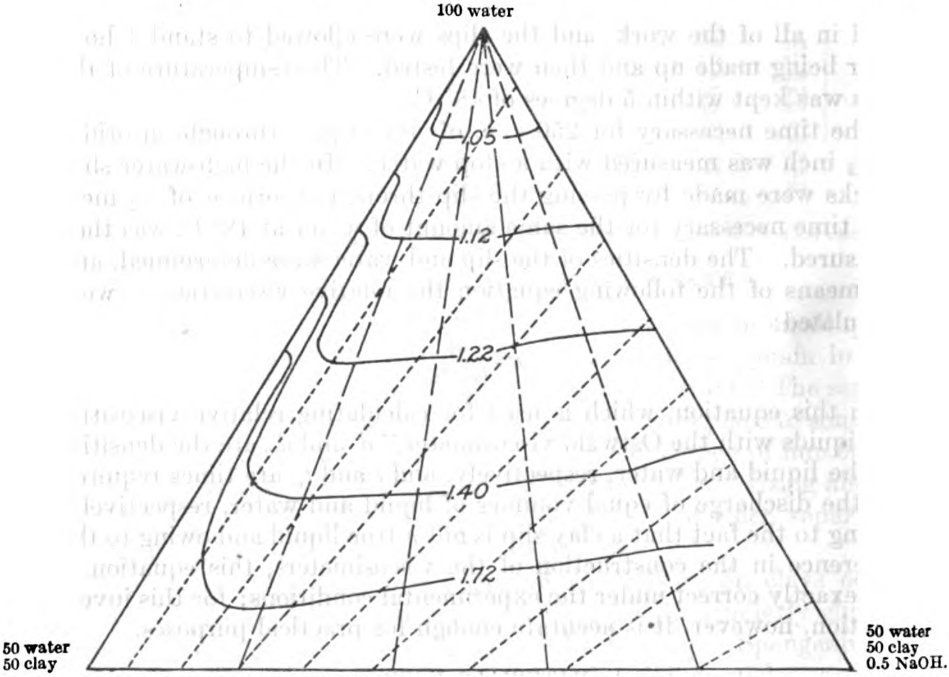

Figure 1.—Georgia kaolin and NaOH. —— equals ratio of NaOH to clay; ------ equals ratio of NaOH to water.

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[24] Foerster, F. Ueber das Gieszens des Tones: Chem. Ind., Jahrg. 28, 1905, pp. 733–740.

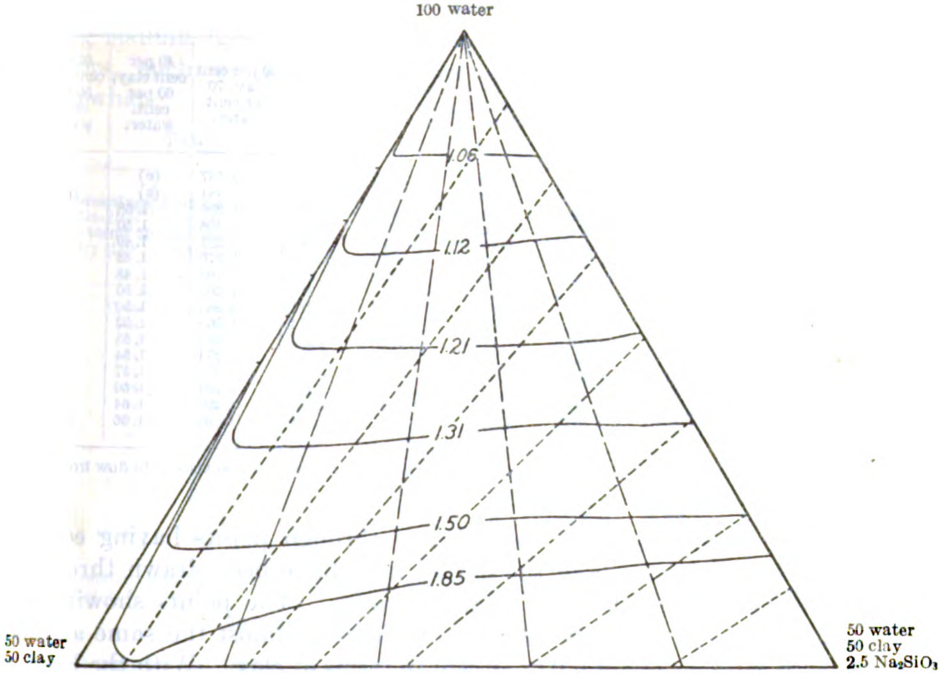

FIGURE 2.—Georgia kaolin and Na_2SiO_3. —— equals ratio of Na_2SiO_3 to clay; ------- equals ratio of Na_2SiO_3 to water.

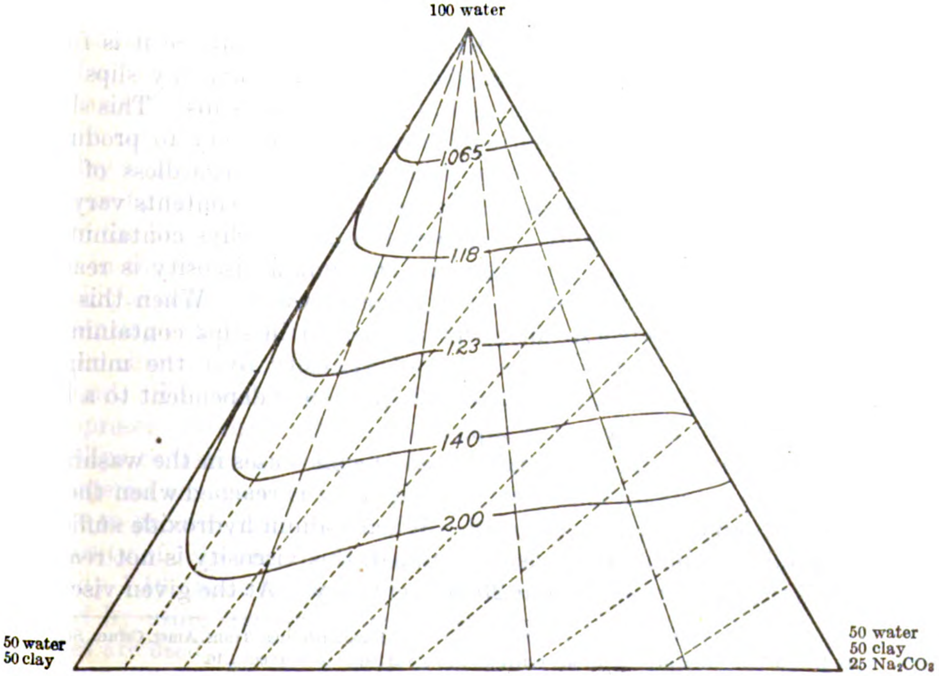

FIGURE 3.—Georgia kaolin and Na_2CO_3. —— equals ratio of Na_2CO_3 to clay; ------ equals ratio of Na_2CO_3 to water.

TABLE 2.—*Viscosity of Georgia kaolin with sodium hydroxide.*

No.	Percentage NaOH in terms of dry clay.	5 per cent clay, 95 per cent water.	10 per cent clay, 90 per cent water.	15 per cent clay, 85 per cent water.	20 per cent clay, 80 per cent water.	25 per cent clay, 75 per cent water.	30 per cent clay, 70 per cent water.	40 per cent clay, 60 per cent. water.	50 per cent clay, 50 per cent. water.
1	0.00	1.032	1.098	1.199	1.391	1.722	2.587	(a)	(a)
2	.06	1.032	1.092	1.189	1.323	1.675	1.984	(a)	(a)
3	.08	1.028	1.066	1.123	1.198	1.250	1.306	1.58	5.87
4	.10	1.027	1.066	1.112	1.175	1.227	1.306	1.50	2.20
5	.12	1.028	1.066	1.112	1.163	1.214	1.281	1.49	2.00
6	.18	1.025	1.066	1.112	1.163	1.214	1.270	1.48	1.93
7	.26	1.026	1.066	1.113	1.167	1.214	1.263	1.48	1.95
8	.34	1.025	1.066	1.113	1.165	1.214	1.263	1.50	2.04
9	.42	1.025	1.065	1.113	1.165	1.214	1.263	1.50	2.10
10	.50	1.025	1.065	1.113	1.166	1.214	1.268	1.52	2.28
11	.58	1.025	1.065	1.114	1.166	1.224	1.269	1.53	2.48
12	.66	1.025	1.064	1.112	1.170	1.224	1.274	1.54	2.81
13	.74	1.025	1.065	1.113	1.175	1.228	1.276	1.57	3.27
14	.80	1.025	1.065	1.112	1.175	1.229	1.281	1.60	3.78
15	.90	1.025	1.065	1.118	1.175	1.236	1.295	1.64	11.03
16	1.00	1.025	1.071	1.118	1.175	1.239	1.307	1.66	(a)

[a] The relative viscosities of these could not be determined as the slips were too viscous to flow from the viscosimeter.

The dash lines have been drawn through points having equal alkali to clay ratios, and the dotted lines have been drawn through points having equal alkali to water ratios. The points showing a sudden drop in viscosity follow a line having almost the same alkali to clay ratio, or about 0.07 per cent in terms of clay. With the high-clay slips slightly more than 0.08 per cent is necessary to produce this drop, owing perhaps to the fact that the electrolyte is not as highly ionized as it is in the more dilute solutions. In following the dotted lines from the high-clay slips to the low-clay substance it is found that points showing minimum viscosity in the high-clay slips pass to points showing a rethickening in the high-water slips. This shows that the practice of calculating the alkalies necessary to produce a certain degree of dispersion in terms of water regardless of how much clay is present is wrong if the clay and water contents vary and if the water is fairly pure. For instance, in the slips containing 50 per cent clay and 50 per cent water, minimum viscosity is reached when the alkali is 0.18 per cent in terms of water. When this concentration of electrolyte in water is reached in slips containing 15 per cent clay, a decided increase of viscosity over the minimum occurs, indicating that the state of dispersion is dependent to a large extent upon the clay in the slip.

A viscosity of 1.16 [25] is maintained in some cases in the washing of clays. If no alkalies are used this viscosity is reached when the slip contains about 13 per cent clay. When sodium hydroxide sufficient to produce minimum viscosity is added, this viscosity is not reached until the slip contains about 20 per cent clay. At the given viscosity about 54 per cent more clay per volume of slip can be treated by using sodium hydroxide than without using any alkalies. Other factors, such as weather conditions, would vary these figures somewhat.

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[25] A viscosity of 1.068 is recommended by Sproat, I. E. Kaolin refining: Trans. Amer. Ceram. Soc., vol. 18, 1916, p. 778. After making density corrections this was found to be about 1.16.

TABLE 3.—*Viscosity of Georgia kaolin with sodium silicate.*

No.	Percentage Na_2SiO_3 in terms of dry clay.	5 per cent clay, 95 per cent water.	10 per cent clay, 90 per cent water.	15 per cent clay, 85 per cent water.	20 per cent clay, 80 per cent water.	25 per cent clay, 75 per cent water.	30 per cent clay, 70 per cent water.	40 per cent clay, 60 per cent water.	50 per cent clay, 50 per cent water.
1..	0.00	1.032	1.098	1.199	1.391	1.722	2.587	(a)	(a)
2..	.08	1.028	1.081	1.150	1.231	1.386	1.708	1.91	(a)
3..	.12	1.025	1.060	1.123	1.210	1.345	1.478	1.53	(a)
4..	.14	1.025	1.061	1.118	1.180	1.310	1.392	1.49	(a)
5..	.16	1.025	1.061	1.112	1.163	1.261	1.306	1.48	3.02
6..	.18	1.025	1.061	1.108	1.158	1.231	1.270	1.46	2.13
7..	.20	1.025	1.061	1.108	1.151	1.220	1.270	1.46	....
8..	.22	1.025	1.061	1.106	1.149	1.220	1.270	1.46	1.88
9..	.26	1.025	1.061	1.103	1.149	1.214	1.270	1.46	....
10..	.30	1.025	1.061	1.103	1.149	1.214	1.270	1.46	1.88
11..	1.00	1.025	1.061	1.103	1.153	1.220	1.270	1.48	2.16
12..	2.00	1.025	1.061	1.103	1.154	1.220	1.231	1.53	2.68
13..	5.00	1.025	1.061	1.103	1.156	1.227	1.295	1.58	3.55
14..	7.00	1.025	1.061	1.103	1.156	1.227	1.302	(a)	(a)
15..	10 00	1.025	1.061	1.103	1.157	1.227	1.308	(a)	(a)

[a] The relative viscosities of these could not be determined as the slips were too viscous to flow from the viscosimeter.

SODIUM SILICATE AND GEORGIA KAOLIN.

The results of adding sodium silicate to Georgia kaolin are shown in Table 3 and figure 2. A decrease to minimum viscosity follows the addition of about .25 per cent of sodium silicate in terms of clay. This electrolyte does not thicken the slip as readily as sodium hydroxide when more electrolyte than is required to produce minimum viscosity is added. Sodium silicate produces a slightly greater drop in viscosity than sodium hydroxide.

Here again the point of minimum viscosity is less defined in the low-clay slips than in the high-clay slips. In following the dotted lines (see fig. 2), representing equal salt to water ratios, from the high-clay to the low-clay slips, it is seen that points showing minimum viscosity in the high-clay slips pass through points showing slight signs of rethickening in the low-clay slips. In following the dash lines representing equal salt to clay ratios from the high-clay to the low-clay slips, no change from minimum viscosity to a rethickening of slip can be found. The sharp drop to minimum viscosity follows closely a line representing equal salt to clay ratios.

In slips containing no alkalies a viscosity of 1.16 is reached when the material contains about 13 per cent clay. When enough sodium silicate to produce minimum viscosity is used the slip does not reach a viscosity of 1.16 until it contains about 20.5 per cent clay. At the viscosity 1.16 about 58 per cent more clay per volume of slip can be treated by using sodium silicate as compared to a slip in which no alkalies are used.

SODIUM CARBONATE AND GEORGIA KAOLIN.

The effect of sodium carbonate on Georgia kaolin is shown in Table 4 and figure 3. The slip reaches minimum viscosity when about .60 per cent alkali in terms of clay is added. Slightly more than this per cent is necessary in the high-clay slips, probably because the electrolyte is more concentrated and hence not as highly ionized as in the high-water slips. It is obvious that sodium carbonate is much "weaker" chemically than sodium hydroxide or sodium silicate because the drop in viscosity is much less, and the amount necessary to produce minimum viscosity is much greater than is necessary with the other two electrolytes.

In going from the high-clay slips to the low-clay the dotted lines representing equal salt to water ratios again pass from points of minimum viscosity in the high-clay through points showing rethickening in the high-water slips. In following in a similar way the dash lines representing equal salt to clay ratios, no change from minimum viscosity to a rethickening can be detected.

TABLE 4.—*Viscosity of Georgia kaolin with sodium carbonate.*

No.	Percentage Na_2CO_3 in terms of dry clay.	5 per cent clay, 95 per cent water.	10 per cent clay, 90 per cent water.	15 per cent clay, 85 per cent water.	20 per cent clay, 80 per cent water.	25 per cent clay, 75 per cent water.	30 per cent clay, 70 per cent water.	35 per cent clay, 65 per cent water.	40 per cent clay, 60 per cent water.	50 per cent clay, 50 per cent water.
1	0.00	1.032	1.098	1.199	1.391	1.722	2.587	(a)	(a)	(a)
2	.04	1.031	1.083	1.177	1.219	1.386	2.070	(a)	(a)	(a)
3	.08	1.031	1.079	1.160	1.208	1.333	1.537	(a)	(a)	(a)
4	.12	1.030	1.073	1.144	1.202	1.280	1.428	1.92	3.17	(a)
5	.16	1.030	1.067	1.133	1.190	1.264	1.387	1.83	2.45	(a)
6	.20	1.029	1.067	1.123	1.176	1.251	1.355	1.78	2.10	(a)
7	.22	1.029	1.067	1.111	1.176	1.243	1.353	1.73	1.91	(a)
8	.24	1.031	1.067	1.107	1.170	1.238	1.337	1.62	1.91	(a)
9	.26	1.030	1.066	1.108	1.170	1.231	1.320	1.54	1.83	(a)
10	.30	1.029	1.066	1.108	1.168	1.231	1.300	1.51	....	4.56
11	.34	1.029	1.065	1.108	1.165	1.220	1.289	1.43	1.65	3.92
12	.40	1.028	1.064	1.108	1.163	1.215	1.283	1.40	1.61	3.65
13	.70	1.028	1.065	1.108	1.164	1.215	1.283	1.40	1.55	3.48
14	1.00	1.028	1.066	1.108	1.167	1.220	1.289	1.42	1.58	5.66
15	2.00	1.028	1.066	1.109	1.171	1.231	1.307	1.46	1.70	(a)
16	3.00	1.029	1.071	1.112	1.174	1.238	1.337	1.51	1.85	(a)
17	4.00	1.029	1.072	1.114	1.179	1.243	1.368	1.62	2.90	(a)
18	5.00	1.029	1.074	1.118	1.182	1.250	1.415	1.84	4.02	(a)

[a] The relative viscosities of these could not be determined as the slips were too viscous to flow from the viscosimeter.

In slips containing no alkalies a viscosity of 1.16 is reached again when the slip contains about 13 per cent clay. If the amount of sodium carbonate necessary to produce minimum viscosity is added, the slip does not reach this viscosity until it contains about 20 per cent clay. At the above viscosity it is therefore possible to treat about 50 per cent more clay by using sodium carbonate than when no alkalies are used.

SODIUM HYDROXIDE AND KENTUCKY BALL CLAY.

Table 5 and figure 4 show the effect of sodium hydroxide on Kentucky ball clay. The point of minimum viscosity is reached when about 0.14 per cent sodium hydroxide in terms of clay is added. The thickening of the slip upon adding more electrolyte than the amount necessary to produce minimum viscosity is more marked in this clay than in the Georgia kaolin.

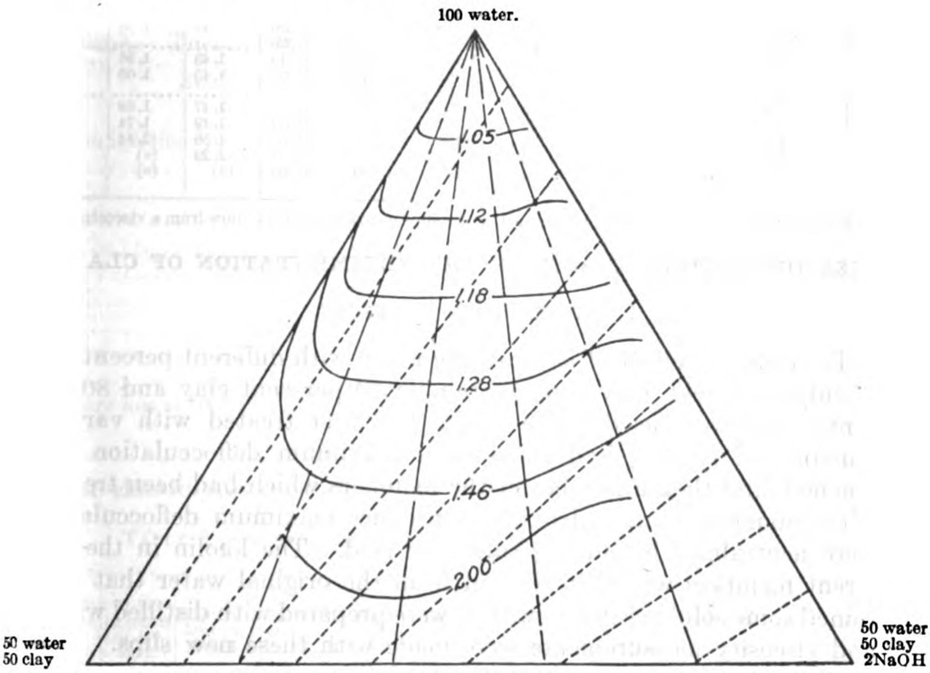

FIGURE 4.—Effect of NaOH on viscosity of Kentucky ball clay. —— equals ratio of NaOH to clay; ------ equals ratio of NaOH to water.

Here again the dotted lines leading from high-clay to low-clay slips pass from points showing minimum viscosity to points showing a flocculation of the slip.

The viscosity 1.16 is reached in a slip containing no alkali when it contains about 13 per cent clay. When sodium hydroxide is used this viscosity is not reached until the slip contains about 20 per cent clay. By using sodium hydroxide about 54 per cent more clay can be treated before the viscosity 1.16 is reached than when no alkalies are used.

TABLE 5.—*Viscosity of Kentucky ball clay with sodium hydroxide.*

No.	Percentage NaOH in terms of dry clay.	5 per cent clay, 95 per cent water.	10 per cent clay, 90 per cent water.	15 per cent clay, 85 per cent water.	20 per cent clay, 80 per cent water.	25 per cent clay, 75 per cent water.	30 per cent clay, 70 per cent water.	35 per cent clay, 65 per cent water.	40 per cent clay, 60 per cent water.	50 per cent clay, 50 per cent water.
1	0.00	1.036	1.090	1.201	1.333	1.700	(a)	(a)	(a)	(a)
2	.04	1.031	1.080	1.123	1.168	1.260	1.391	1.88	(a)	(a)
3	.08	1.030	1.072	1.122	1.165	1.240	1.320	1.45	1.73	7.81
4	.10	1.030	1.072	1.123	1.163	1.242	1.320	....	....	....
5	.12	1.030	1.072	1.122	1.160	1.242	1.320	1.44	1.53	2.25
6	.14	1.029	1.073	1.123	1.160	1.242	1.320	....	....	....
7	.16	1.029	1.073	1.122	1.161	1.242	1.319	1.43	1.56	....
8	.18	1.029	1.075	1.122	1.161	1.242	1.321	1.45	1.60	2.23
9	.20	1.029	1.075	1.122	1.162	1.244	1.321	....	....	....
10	.22	1.029	1.075	1.122	1.162	1.245	1.322	1.47	1.68	3.31
11	.26	1.029	1.075	1.122	1.162	1.247	1.344	1.49	1.74	(a)
12	.30	1.029	1.077	1.130	1.166	1.259	1.368	1.56	2.44	(a)
13	.34	1.031	1.077	1.133	1.168	1.276	1.451	2.29	(a)	(a)
14	.38	1.031	1.075	1.132	1.185	1.290	1.501	(a)	(a)	(a)

[a] Relative viscosities could not be determined, as the slips were too viscous to flow from a viscosimeter.

USE OF SULPHURIC ACID IN THE SEDIMENTATION OF CLAYS.

DESCRIPTION OF TESTS.

To study the effect of neutralizing a slip with different percentages of sulphuric acid, clay slips containing 20 per cent clay and 80 per cent water were used. The kaolin was first treated with varying amounts of sodium hydroxide until maximum deflocculation was reached, and then a number of the members which had been treated with enough sodium hydroxide to produce maximum deflocculation were neutralized by adding sulphuric acid. The kaolin in the different members was then filtered from the original water that contained some soluble salts, new slips were prepared with distilled water, and viscosity measurements were made with these new slips. This procedure gave a comparison between the clays before and after filter pressing.

In order to study the effect of alkalies on the viscosity of kaolins treated with different proportions of sulphuric acid, the kaolin was first deflocculated with sodium hydroxide, neutralized or partly neutralized with different amounts of sulphuric acid, and filtered. The clay samples thus treated were then deflocculated with varying amounts of sodium hydroxide and their viscosity measured.

The degree of sedimentation was studied by placing the freshly treated slips in tall glass tubes and at the end of 24 and 72 hours, respectively, the height of the kaolin was measured and expressed in terms of the total height of the slip as the percentage height of clay in the slip.

One-inch cubes were molded with 50 parts of filtered kaolin and 50 parts of potter's flint, and after the cubes had dried in air their color was observed. Some of the cubes were made with all kaolin, and their

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color was also observed when dry. The cubes containing 50 per cent flint were finally dried at 110° C., and the time necessary for disintegration in water at room temperature was measured for each cube.

MATERIALS STUDIED.

To study the effect of sulphuric acid on the sedimentation of kaolin three clays were studied, namely: (1) a kaolin from Gordon, Ga., (2) a kaolin from Edgar, Fla., and (3) Iotla kaolin from North Carolina. Their chemical analyses are as follows:

Analyses of Georgia, Florida, and North Carolina kaolin.

	1.	2.	3.
Loss on ignition	13.63	14.86	16.54
SiO_2	44.25	45.67	45.17
Al_2O_3	38.06	38.45	37.35
Fe_2O_3	1.03	.75	.60
CaO	.08	......	Trace.
MgO	Trace.	.05	Trace.
TiO_2	1.29	.10	.03
Na_2O	.10	......	......
K_2O	.70	.06	.70
S	.06	......	......
Moisture loss at 105° C	.38	1.50	3.35
	99.58	99.94	100.39

The electrolytes used were c. p. NaOH, and H_2SO_4.

TABLE 3.—*Georgia kaolin with sodium hydroxide and sulphuric acid.*

NaOH in terms of dry clay.	H_2SO in terms of dry clay.	Equivalents of NaOH.	Equivalents of H_2SO_4.	Viscosity of unfiltered clay.	Viscosity of filtered clay.	Time of disintegration, minutes.	Height of clay, 24 hours.	Height of clay, 72 hours.	Appearance of water above clay.	Color of dry filtered clay.
Per cent.	*Per cent.*	*Per cent.*	*Per cent.*				*Per cent.*	*Per cent.*		
0.00	0.000	0.00	0.00	1.391	1.335	5.5	66.0	50.0	Clear....	White.
.06	.000	.24	.00	1.323	1.375	....	76.0	69.0	...do.....	Do.
.08	.000	.32	.00	1.198	1.320	110.0	98.0	97.5	Turbid..	Do.
.10	.000	.40	.00	1.175	1.169	115.0	98.0	97.5	...do.....	Do.
.12	.000	.48	.00	1.163	1.163	106.0	98.0	97.5	...do.....	Do.
.18	.000	.72	.00	1.163	1.163	110.0	98.0	97.5	...do.....	Do.
.18	.056	.72	.18	1.173	1.163	82.0	97.8	97.5	...do.....	Do.
.18	.111	.72	.36	1.200	1.250	31.0	86.8	68.5	...do.....	Do.
.18	.166	.72	.54	1.395	1.395	5.8	88.0	63.3	Clear....	Do.
.18	.221	.72	.72	1.395	1.355	5.8	80.0	62.8	...do.....	Faint gray.
.18	.307	.72	1.00	1.390	1.310	5.3	80.0	56.2	...do.....	Gray.

RESULTS OF TESTS.

SULPHURIC ACID AND GEORGIA KAOLIN.

With Georgia kaolin the state of maximum deflocculation was reached when 0.72 per cent of one equivalent (0.288 gram) of sodium hydroxide was added to the slip containing 160 grams of clay and 640 grams of water.

Examination of the viscosity table and curves of the unfiltered clay (see Table 6 and fig. 5) shows that upon neutralizing the sodium hydroxide with sulphuric acid the increase in viscosity is at first very slight until 0.38 per cent equivalents of acid are added, when viscosity suddenly rises from 1.174 to 1.370. The viscosity curve of the filtered clay seems to be close to that of the unfiltered clay, except when an excess of sulphuric acid has been added, and then it seems to be lower. A little of the fine deflocculated clay passed through even the finest filter paper.

By examination of the curve representing the percentage height of kaolin after 24 hours, it appears that the untreated kaolin settled 34 per cent, whereas the kaolin that had been treated with .72 per cent equivalent of sodium hydroxide and an equivalent amount sulphuric acid settled only 20 per cent. After allowing the slip to stand 72 hours the untreated kaolin settled 50 per cent whereas the slip neutralized with an equivalent amount of sulphuric acid settled 37.2 per cent. Evidently a slip of kaolin treated with alkalies and sulphuric acid should be allowed to settle a much longer time than a slip of untreated clay.

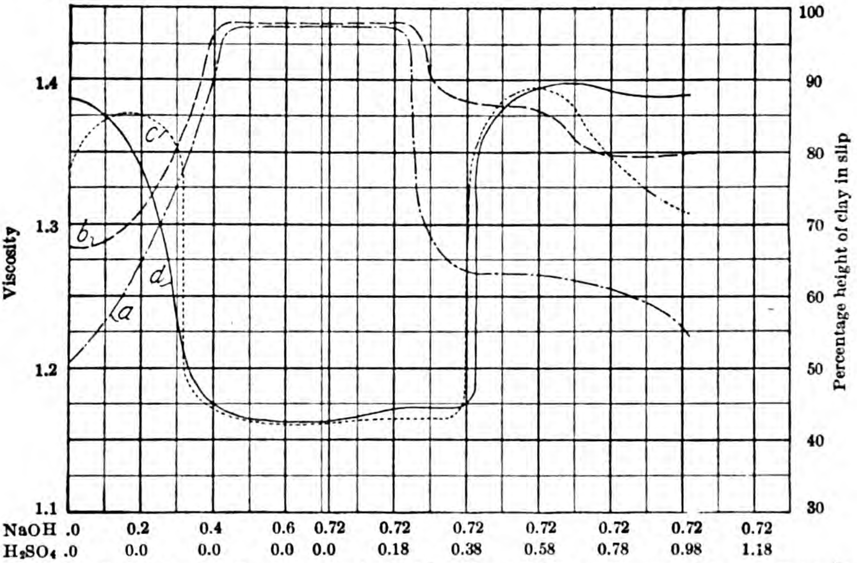

FIGURE 5.—Georgia kaolin. Per cent equivalents of NaOH and H_2SO_4 to 160 grams of clay. *a*, Height of clay after 72 hours; *b*, height of clay after 24 hours; *c*, viscosity of unfiltered clay; *d*, viscosity of filtered clay.

The cubes with 50 per cent kaolin and 50 per cent flint were allowed to dry in air for 5 days. Cubes made with the deflocculated kaolin appeared to be whiter than the untreated kaolin and very fine grained. Upon adding sulphuric acid the color remains white until the amount of sulphuric acid becomes equivalent to the sodium hydroxide originally used, when the color becomes a slightly bluish gray, probably due to the charring effect of the excess H_2SO_4 on the organic matter present. Upon adding more sulphuric acid the color becomes decidedly darker. The dark discoloration was not as pronounced in the cubes of all clay as it was in the cubes containing 50 per cent flint. In the latter the discoloration seems due to adding too much sulphuric acid, as an amount less than the equivalent of sodium hydroxide gives the best white color.

The time of disintegration in water of the untreated kaolin is 5.5 minutes and that of the deflocculated kaolin is 110 minutes.

SULPHURIC ACID AND FLORIDA KAOLIN.

Florida kaolin reached the state of maximum deflocculation when 1 per cent of one equivalent of sodium hydroxide was added to a slip containing 160 parts of kaolin and 640 parts of water.

TABLE 7.—*Florida kaolin with sodium hydroxide and sulphuric acid.*

NaOH in terms of dry clay.	H_2SO_4 in terms of dry clay.	Equivalents of NaOH.	Equivalents of H_2SO_4.	Viscosity of unfiltered clay.	Viscosity of filtered clay.	Time of disintegration, minutes.	Height of clay, 24 hours.	Height of clay, 72 hours.	Appearance of water above clay.	Color of dry filtered clay.
Per cent.	*Per cent.*	*Per cent.*	*Per cent.*				*Per cent.*	*Per cent.*		
0.00.....	0.000	0.00	0.00	1.187	1.201	4.8	51.5	41.3	Clear...	White.
.05.....	.000	.20	.00	1.230	1.248	6.1	70.5	63.5	...do....	Do
.10.....	.000	.40	.00	1.170	1.200	10.3	90.0	86.0	Turbid..	Do.
.15.....	.000	.60	.00	1.140	1.175	19.2	97.5	97.0	...do....	Do.
.20.....	.000	.80	.00	1.140	1 173	32.8	98.5	98.0	.. do....	Do.
.25.....	.000	1.00	.00	1.139	1.180	31.7	98.5	98.0	...do....	Do.
.25.....	.077	1.00	.25	1.158	1.180	21.0	96.0	95.0	...do....	Do.
.25.....	.154	1.00	.50	1.238	1.196	10.0	93.4	80.0	...do....	Do.
.25.....	.231	1.00	.75	1.283	1.328	8.0	91.6	79.8	Slightly turbid.	Do.
.25.....	.307	1.00	1.00	1.306	1.358	6.1	91.6	73.6	Clear....	Do.
.25.....	.460	1.00	1.50	1.345	1.380	5.5	94.8	68.7	...do....	Do.

With small additions of sodium hydroxide (see Table 7 and fig. 6), the viscosity of the slip increases and with larger additions it decreases. This increase may be due to the presence of soluble calcium salts[26] which are converted into soluble calcium hydroxide on the addition of sodium hydroxide. Upon adding sulphuric acid it is seen that the increase in viscosity is at first small until between .25 and .50 per cent of one equivalent of acid is added, when the viscosity suddenly rises from 1.158 to 1.238. When sulphuric acid equivalent to the sodium hydroxide is added, the viscosity becomes 1.306, which is much higher than it was for the untreated clay. The increase in plasticity that sometimes has caused trouble to kaolin refiners is undoubtedly due to this increase in viscosity; it can be reduced by adding less sulphuric acid. For instance, the viscosity 1.187, which is the viscosity of the untreated clay, is reached when .42 per cent of one equivalent of sulphuric acid is added. The viscosities of the filtered kaolin appear higher than those of the unfiltered clay.

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[26] Foerster, F. Ueber das Gieszen des Tones: Chem. Ind., Jahrg. 28, 1905, pp. 733–740.

Examination of the curve that represents the height of kaolin in the slip after 24 hours shows that the clay has settled only 8.4 per cent after the chemical treatment; in the same slip, before it was treated, the kaolin settled 48.5 per cent. After 72 hours the untreated kaolin settled 58.7 per cent, whereas the slip neutralized with an equivalent amount of sulphuric acid settled 26.4 per cent. Here again it will be necessary to allow the chemically treated slip to settle for a longer time than was necessary for the untreated slip. Whether some other reagent will act better than sulphuric acid in this respect is not known.

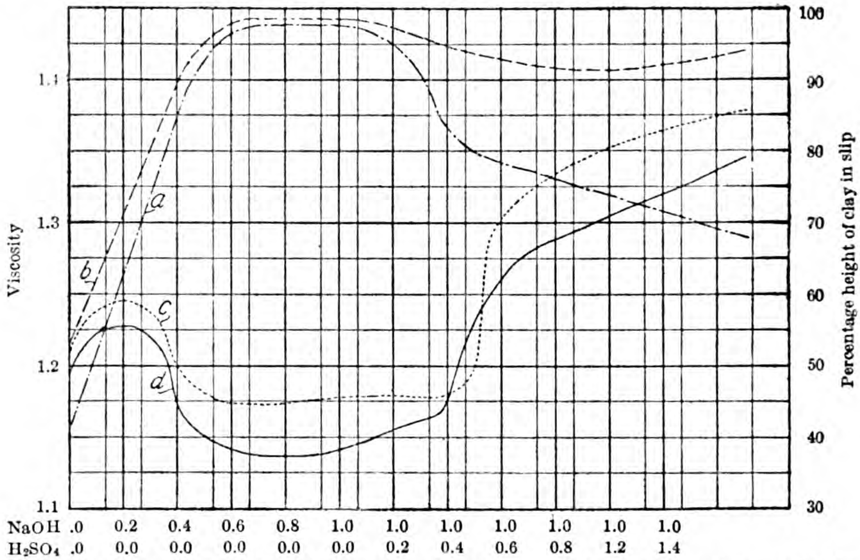

FIGURE 6.—Florida kaolin. Per cent equivalents of NaOH and H_2SO_4 to 160 grams of clay: *a*, Height of clay after 72 hours; *b*, height of clay after 24 hours; *c*, viscosity of filtered clay; *d*, viscosity of unfiltered clay.

The kaolin treated with an excess of sulphuric acid showed no black discoloration; some clays, therefore, are not discolored by adding a slight excess of acid.

The time of disintegration in water of the untreated kaolin is 4.8 minutes; for the deflocculated kaolin it is 31.7 minutes. Upon neutralizing the sodium hydroxide with acid the time became 6.1 minutes.

SULPHURIC ACID AND NORTH CAROLINA KAOLIN.

North Carolina kaolin was deflocculated with .8 per cent of one equivalent of sodium hydroxide added to a slip containing 160 grams of clay and 640 grams of water.

TABLE 8.—*North Carolina kaolin with sodium hydroxide and sulphuric acid.*

NaOH in terms of dry clay.	H_2SO_4 in terms of dry clay.	Equivalents of NaOH.	Equivalents of H_2SO_4.	Viscosity of unfiltered clay.	Viscosity of filtered clay.	Time of disintegration, minutes.	Height of clay, 24 hours.	Height of clay, 72 hours.	Appearance of water above clay.	Color of dry filtered clay.
Per cent.	*Per cent.*	*Per cent.*	*Per cent.*				*Per cent.*	*Per cent.*		
0.00	0.000	0.0	0.00	1.180	1.195	5.8	34.4	32.7	Clear....	Light gray.
.05	.000	.2	.00	1.154	1.190	7.7	35.9	32.0	...do.....	Do.
.10	.000	.4	.00	1.150	1.163	8.2	98.0	97.0	...do.....	Do.
.15	.000	.6	.00	1.151	1.161	11.2	98.0	97.0	...do.....	Do.
.20	.000	.8	.00	1.151	1.157	16.4	98.0	97.0	...do.....	Do.
.20	.062	.8	.20	1.153	1.157	11.0	97.8	96.0	...do.....	Faint gray.
.20	.123	.8	.40	1.168	1.157	8.9	35.0	30.0	...do.....	Light gray.
.20	.184	.8	.60	1.175	1.169	7.5	35.2	30.0	...do.....	Do.
.20	.246	.8	.80	1.186	1.183	6.5	36.0	32.4	...do.....	Gray.
.20	.385	.8	1.25	1.192	1.200	4.6	37.2	33.8	...do.....	Do.

The viscosity of the slip before treatment is 1.180 and after the addition of an equivalent amount of acid is 1.186. The filtered clay has a viscosity slightly higher than the unfiltered clay. (See Table 8 and fig. 7.)

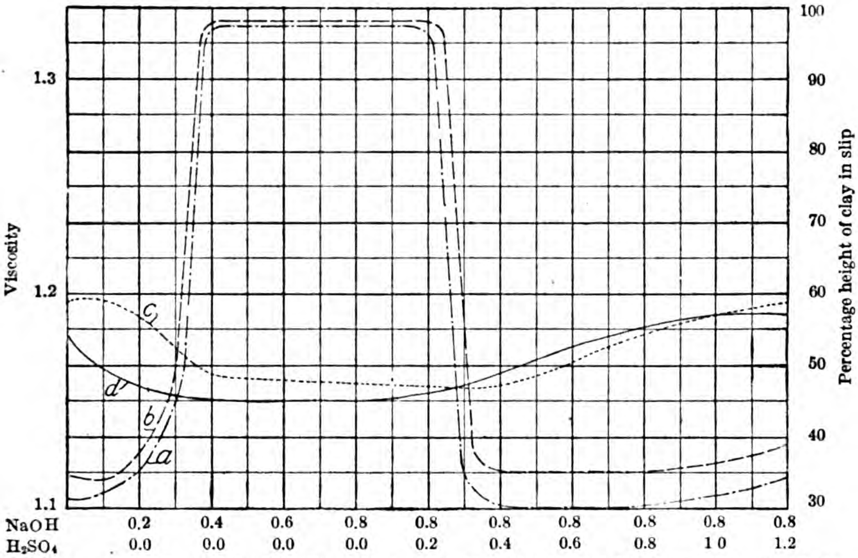

FIGURE 7.—North Carolina kaolin. Per cent equivalents of NaOH, and H_2SO_4 to 160 grams of clay. *a*, Height of clay after 72 hours; *b*, height of clay after 24 hours; *c*, viscosity of filtered clay; *d*, viscosity of unfiltered clay.

The curve representing the height of clay in the slip shows that the settle after an equivalent amount of acid is added is about the same as for the untreated kaolin. Twenty-four hours is time enough for settling this kaolin.

The untreated clay upon drying showed a dark color. That color became less apparent when the kaolin was deflocculated, but when an amount of acid equivalent or more than equivalent to the sodium hydroxide is added the black scumming appears much more pronounced than on the untreated kaolin.

The time of disintegration in water for the deflocculated kaolin was again greater than for the untreated kaolin.

TREATMENT WITH DIFFERENT AMOUNTS OF SULPHURIC ACID.

The kaolin in each test was treated with 0.72 per cent of one equivalent of sodium hydroxide, which was added to a slip containing 160 grams of clay and 640 grams of water (see Table 9 and fig. 8). Different members were then treated with 0.52, 0.72, and 1 per cent of one equivalent of sulphuric acid, respectively. The clay was then filtered and varying amounts of sodium hydroxide were added. If the larger quantities of sulphuric acid have been used, larger quantities of sodium hydroxide are necessary to produce minimum viscosity in the slip. If an excess of sulphuric acid has been used, the viscosity of the kaolin increases, but when more sodium hydroxide is added the viscosity again decreases to a minimum. The difference in behavior of the kaolin treated with different amounts of sulphuric acid is most pronounced when the additions of alkali are small, and is not very pronounced when larger amounts of alkalies are added.

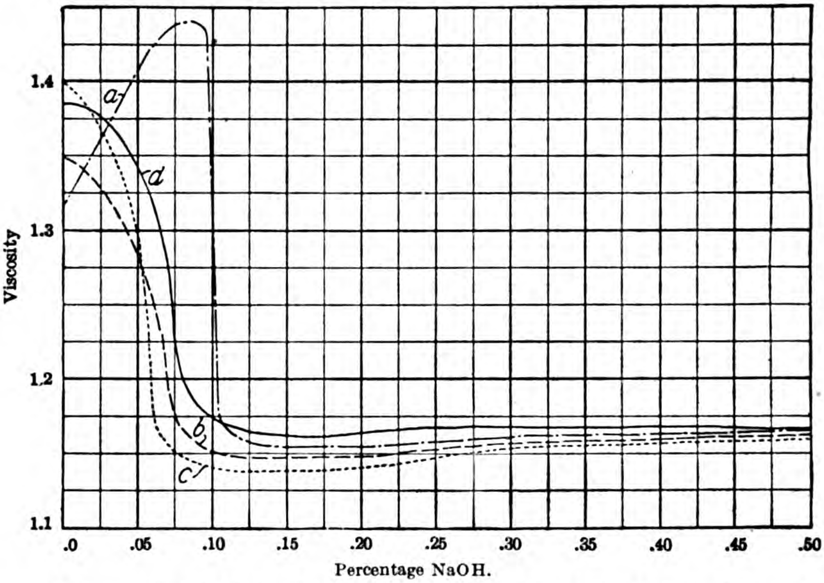

FIGURE 8.—Georgia kaolin. Percentage of NaOH. *a*, Treated with .72 per cent equivalent NaOH and 1.00 per cent equivalent H_2SO_4; *b*, treated with .72 per cent equivalent H_2SO_4; *c*, untreated kaolin; *d*, treated with .72 per cent equivalent NaOH and .54 per cent equivalent H_2SO_4.

TABLE 9.—*Georgia kaolin with different amounts of sulphuric acid.*

No.	NaOH added to filtered clay, in terms of clay.	Untreated clay.	Treated with .72 per cent equivalent of NaOH.		
			Neutralized with .54 per cent equivalent H_2SO_4 and filtered.	Neutralized with .72 per cent equivalent H_2SO_4 and filtered.	Neutralized with 1 per cent equivalent H_2SO_4 and filtered.
1	0.000	1.390	1.387	1.322	1.323
2	.096	1.180	1.248	1.270	1.420
3	.128	1.165	1.142	1.165	1.442
4	.160	1.163	1.143	1.147	1.332
5	.192	1.163	1.142	1.147	1.158
6	.288	1.168	1.142	1.144	1.150
7	.384	1.168	1.145	1.147	1.155
8	.480	1.168	1.155	1.336	1.164
9	.800	1.168	1.162	1.332	1.164

EFFECT OF ELECTROLYTES WHEN ADDED TO PLASTIC BODIES.

DESCRIPTION OF TESTS.

For this part of the investigation the following mixtures were selected:

(1) 50 parts Kentucky ball clay and 50 parts flint.
(2) 50 parts Tennessee ball clay and 50 parts flint.
(3) 50 parts Georgia kaolin and 50 parts flint..
(4) 50 parts Kentucky ball clay and 50 parts grog.
(5) 100 parts Kentucky ball clay.

The cross-breaking strength, water of plasticity, drying shrinkage, density, and porosity were determined for each clay in the raw condition. The tests were made on the untreated clays and on the clays to which 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 1.00, 1.50, 2.00, 3.00, and 5.00 percentages by weight of electrolyte had been added. The electrolytes added were sodium hydroxide, sodium silicate, sodium carbonate, calcium hydroxide, tannic acid, and sulphuric acid.

For the cross-breaking tests, bars 1 by 1 by 7 inches were molded and dried at room temperatures for 3 days, then in a drying oven at 65° C. for 24 hours, and finally at 110° C. for 24 hours. A span of 5 inches was used in breaking the pieces transversely. The modulus of rupture of each piece was calculated, the average of 10 determinations being taken as the final result.

In making the determinations of the water of plasticity and the drying shrinkage the electrolyte was added to a quantity of water slightly less than that required for developing the maximum plasticity. In case the limits for normal consistency were large, the water was added by volume to keep the per cent added as nearly as possible the same, thereby making the shrinkage data more closely comparable.

The drying shrinkage was determined by the kerosene immersion method, using the pycnometer volumeter, and the percentage of volume shrinkage was calculated on the basis of the dry volume.

The percentage shrinkage in terms of the true clay volume was determined by the method described by Bleininger[27], as follows:

$$s=\frac{d(v_1-v_2)}{w}=100.$$

s=percentage volume shrinkage in terms of true clay volume.
d=specific gravity of the powdered clay.
v_1=volume of the clay briquet in the wet condition.
v_2=volume of the clay briquet in the dried condition.
w=weight of the dried briquet.

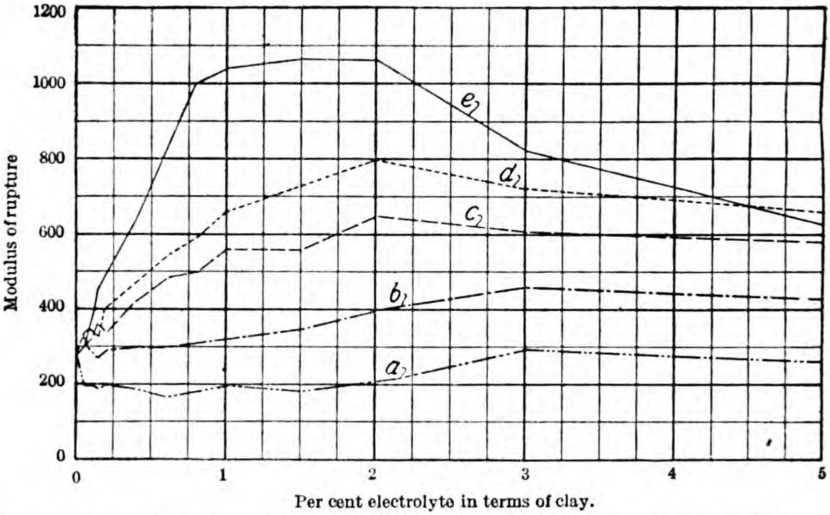

FIGURE 9.—Effect of electrolytes on dry strength of clays and mixtures. Percentage of electrolyte in terms of clay. *a*, H_2SO_4; *b*, tannic acid; *c*, Na_2CO_3; *d*, Na_2SiO_3; *e*, NaOH.

RESULTS OF ADDING ELECTROLYTES TO PLASTIC BODIES.

Figures 9 and 10 show the effect of electrolytes on the dry strength of clays and mixtures studied. The alkalies and tannic acid increase, but sulphuric acid lowers, the strength. Calcium hydroxide improves the strength when added in small proportions (.2 to 2 per cent) and lessens it when added in larger percentages. The maximum effect is produced with alkalies when between .8 and 2.5 per cent is used, and with tannic acid when 3 per cent is employed. When caustic soda was added the bodies containing 50 clay and 50 nonplastic material became very difficult to mold, and would not retain their shape unless a low percentage of water was used; in this condition the clays laminated badly. Lamination was greatest when a maximum strength was produced (see fig. 9) and was less

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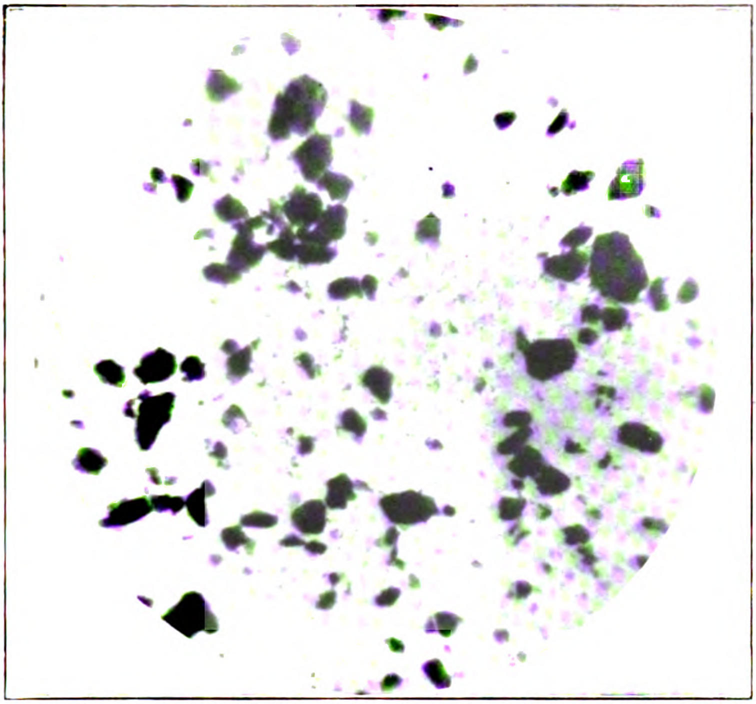
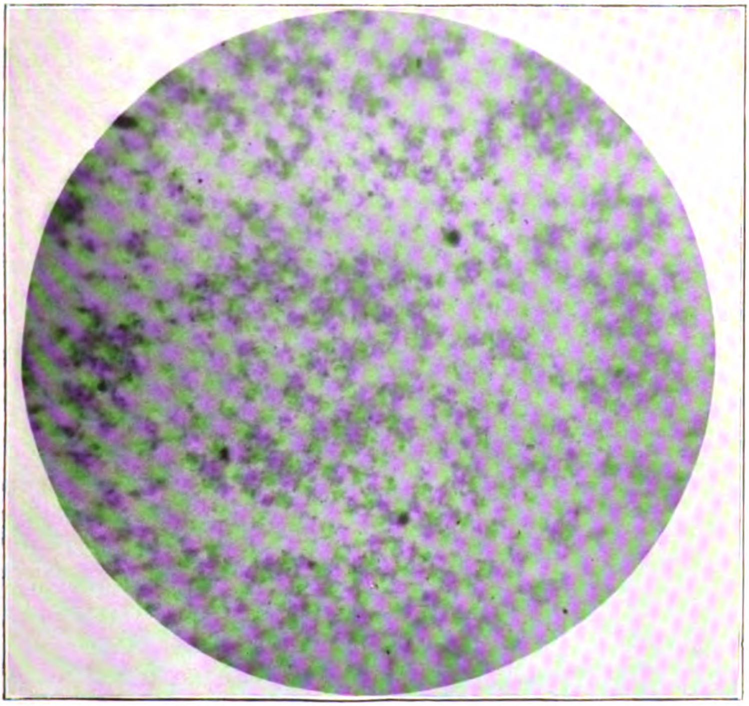
[27] Bleininger, A. V., The effect of preliminary heat treatments upon the drying of clays: Bureau of Standards Tech. Paper 1, 1910, p. 21.



A. UNTREATED TENNESSEE BALL CLAY MAGNIFIED 50 DIAMETERS.



B. TENNESSEE BALL CLAY DEFLOCULATED WITH NaOH, MAGNIFIED 50 DIAMETERS.

noticeable when the bodies had a lower strength. The property of molding poorly was marked when sodium silicate, sodium carbonate, or above 2 per cent sulphuric acid was used, and was scarcely noticed when calcium hydroxide, tannic acid, or bodies containing 100 per cent clay were employed. Less than 2 per cent sulphuric acid produced better moldable bodies than the untreated body.

The ball clays turned from their natural brown color to a black upon the addition of a large percentage of alkalies or acid. When calcium hydroxide was used the clay briquettes retained more of their natural color but formed scales on the surface resembling bark.

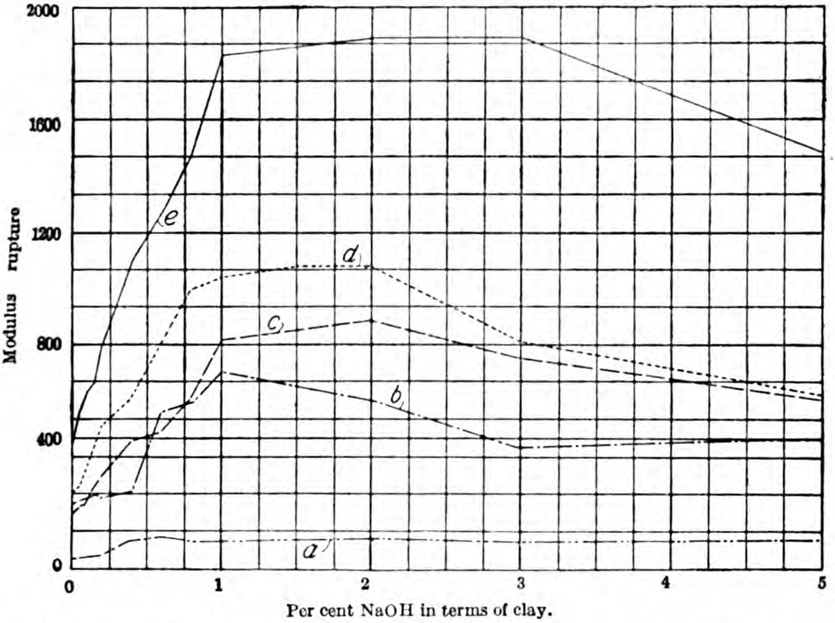


FIGURE 10.—Effect of sodium hydroxide on dry strength of clays and mixtures. Percentage of NaOH in terms of clays: *a*, 50 per cent Georgia kaolin and 50 per cent flint; *b*, 50 per cent Tennessee ball clay and 50 per cent flint; *c*, 50 per cent Kentucky ball clay and 50 per cent grog; *d*, 50 per cent Kentucky ball clay and 50 per cent flint; *e*, Kentucky ball clay.

Under the microscope the clays treated with alkalies consist of very fine grains, as is characteristic of deflocculated clays, but the untreated clay is much coarser. (See Plate I, A, and B.) This deflocculation may explain to some extent the increase in mechanical strength, as the fine grains can pack together more closely and hence make a denser body.

When acids in small percentages are used the effect is the reverse of that produced by alkalies. It appears that the changes produced are functions of the alkalinity or the acidity of the bodies, alkalies increasing the strength and acids decreasing it.

In practically all of the results NaOH proved much more effective than Na_2SiO_3 or Na_2CO_3. NaOH is more highly ionized than Na_2CO_3

(see Table 1, p. 12). The relative effects of the electrolytes may be proportional, therefore, to the relative degree of ionization of the different electrolytes, the so-called "strong" electrolytes of higher degree of ionization being most effective.

Assuming that maximum strength corresponds to minimum viscosity, both representing maximum deflocculation, it is necessary to add 0.16 per cent NaOH in terms of clay in order to produce maximum deflocculation of a slip containing 40 clay and 60 water. To produce maximum strength it is necessary to add 1.5 per cent NaOH in terms of clay when the plastic mass contains 68 clay and 32 water. (See Table 5 and figs. 4 and 10.)

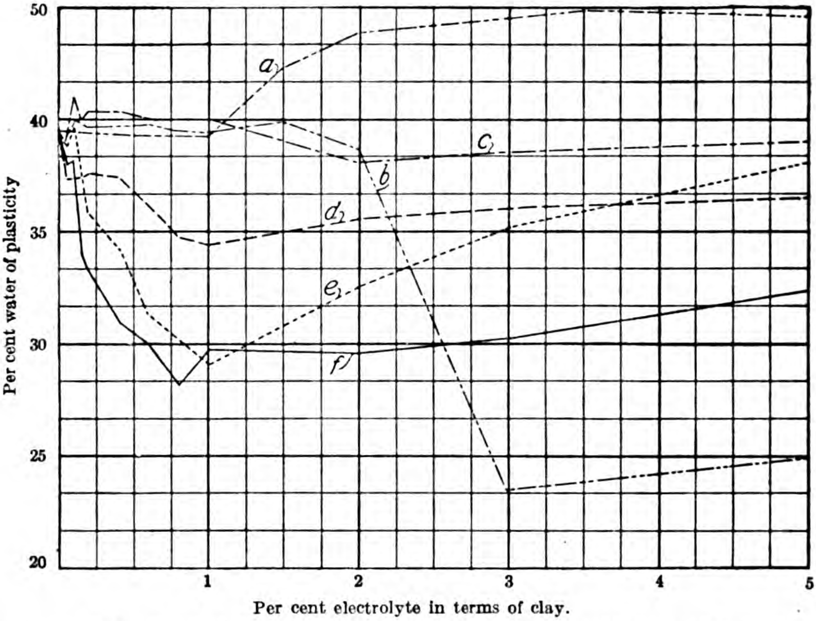


FIGURE 11.—Effect of electrolytes on the water of plasticity in a mixture of 50 per cent Kentucky ball clay and 50 per cent flint. *a*, CaOH; *b*, H_2SO_4; *c*, tannic acid; *d*, Na_2CO_3; *e*, Na_2SiO_3; *f*, NaOH.

In the first place the normal concentration as shown in Table 1 is 0.000666, which has a molecular conductivity of 208. In the second case the concentration is about 0.8 per cent normal with 68 clay and 32 water until all the water has been evaporated, when the normal concentration would increase. The molecular conductivity would range from 164.8 to 0. It is necessary to add five times as much NaOH in terms of clay in order to produce maximum strength on drying as it is necessary to add to produce minimum viscosity in a clay slip containing at first only slightly more water. This fact might be due to a decreased ionization produced in drying in the first slip, hence to reducing chemical activity and increasing the amount of NaOH in terms of clay requisite to produce maximum deflocculation.

WATER OF PLASTICITY.

Figures 11 and 12 show the effect of electrolytes on the water of plasticity. With the two ball clays the alkalies lessen the percentage of water necessary. If a small amount of acid is used a greater amount of water is necessary to work the clays, but if more is added a smaller amount of water must be used. Calcium hydroxide also increases the water of plasticity.

SHRINKAGE IN VOLUME.

Figures 13, 14, and 15 show the effect of electrolytes on the volume shrinkage of clays and mixtures. When 1 per cent alkalies is used there seems to be a decrease in volume shrinkage in all the 50–50 mixtures of clay and flint except with Georgia kaolin; with this the shrinkage becomes greater. In a test of Kentucky ball clay alone there was an increase in shrinkage on the addition of sodium hydroxide. Sulphuric acid in small percentages increases the shrinkage and in larger quantities lowers it. Calcium hydroxide and tannic acid increase the shrinkage.

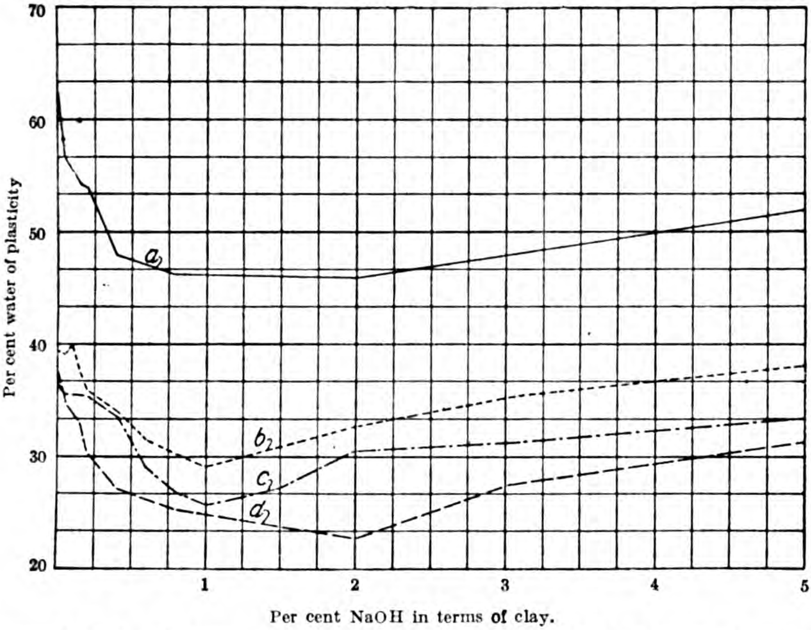


FIGURE 12.—Effect of sodium hydroxide on the water of plasticity of different clays and mixtures. *a*, Kentucky ball clay; *b*, 50 per cent Kentucky ball clay and 50 per cent flint; *c*, 50 per cent Kentucky ball clay and 50 per cent grog; *d*, 50 per cent Tennessee ball clay and 50 per cent flint.

The ratio of pore to shrinkage water becomes lower, though the percentage of shrinkage water in terms of total water becomes higher until 2 per cent caustic soda is added, when the reverse is true. As clays having a low ratio of pore to shrinkage water, and a high

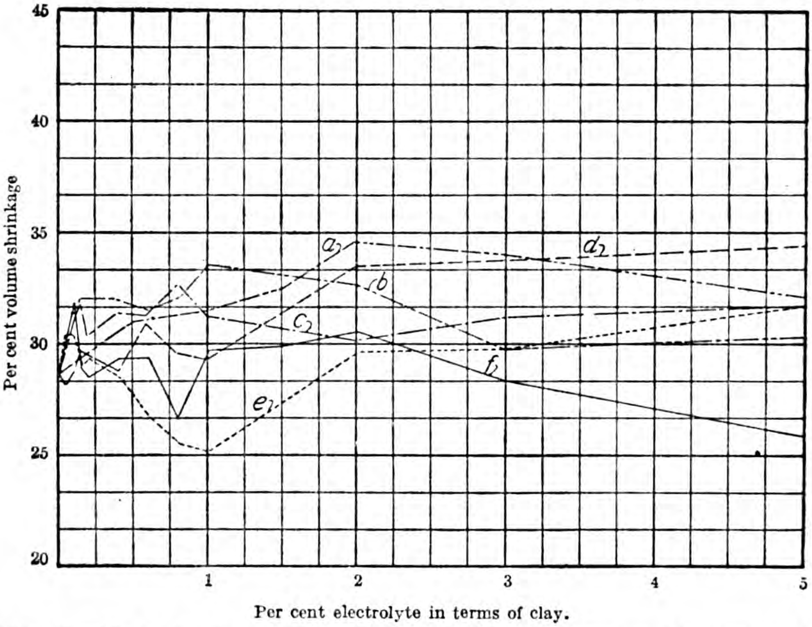


FIGURE 13.—Effect of electrolytes on the volume shrinkage of a mixture of 50 per cent Kentucky ball clay and 50 per cent flint. *a*, CaOH; *b*, H_2SO_4; *c*, tannic acid; *d*, Na_2CO_3; *e*, Na_2SiO_3; *f*, NaOH.

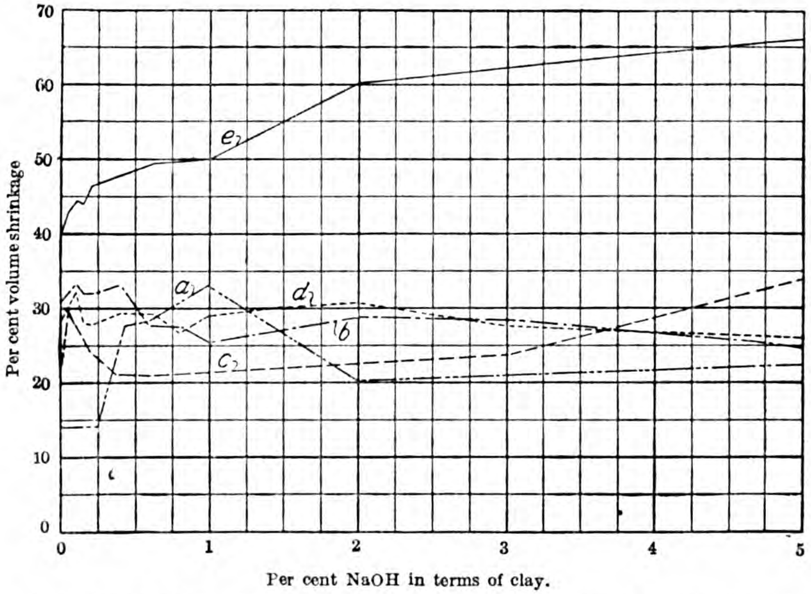


FIGURE 14.—Effect of sodium hydroxide on volume shrinkage. *a*, 50 per cent Georgia kaolin and 50 per cent flint; *b*, 50 per cent Tennessee ball clay and 50 per cent flint; *c*, 50 per cent Kentucky ball clay and 50 per cent grog; *d*, 50 per cent Kentucky ball clay and 50 per cent flint; *e*, Kentucky ball clay.

per cent of shrinkage water in terms of total water, often have good strength, these results are in accordance with the strength tests. (See fig. 9.)

DENSITY.

Figures 16 and 17 show the effect of electrolytes on the dry density of clays and mixtures. The alkalies and tannic acid make the bodies more dense, the maximum effect being produced with from 0.40 to 3 per cent. When more than 2 per cent sulphuric acid is used, the density is increased to a remarkable extent, but in spite of this effect there is only a small improvement in strength (see fig. 9), owing perhaps to the oxidizing effect of sulphuric acid in destroying the organic bond. Calcium hydroxide increases the density until 1 per cent is added, after which it decreases the density.

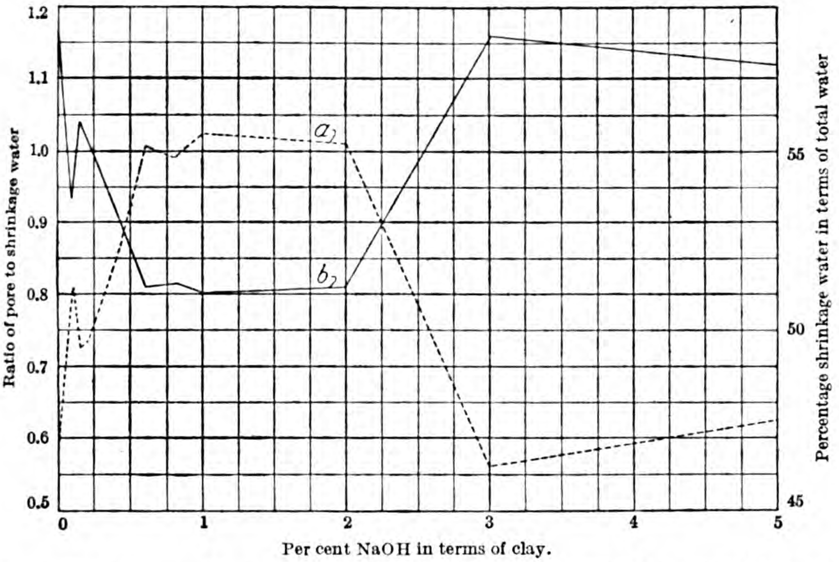


FIGURE 15.—Shrinkage and pore water in a mixture of 50 per cent Kentucky ball clay and 50 per cent flint. *a*, Shrinkage water in terms of total water; *b*, ratio of pore to shrinkage water.

POROSITY.

Figures 18 and 19 show the effect of electrolytes on the porosity of the clays. The porosity is decreased by adding alkalies; acids in small percentages make the body more open, and in larger quantities lower the porosity. Calcium hydroxide makes the body more porous.

FIRING PROPERTIES.

Figure 20 shows the effect of sodium hydroxide on the firing properties of a mixture composed of 50 parts Kentucky ball clay and 50 parts flint after firing to cone 01. The shrinkage in volume is decreased until over 0.8 per cent of NaOH is added, but when

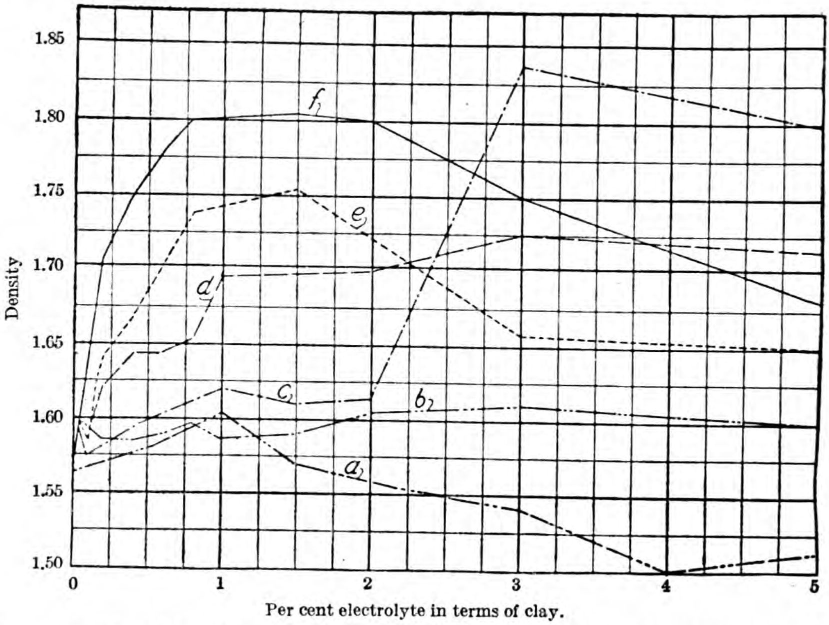


FIGURE 16.—Effect of electrolytes on the dry density of a mixture of 50 per cent Kentucky clay and 50 per cent flint. *a*, CaOH; *b*, tannic acid; *c*, H_2SO_4; *d*, Na_2CO_3; *e*, Na_2SiO_3; *f*, NaOH.

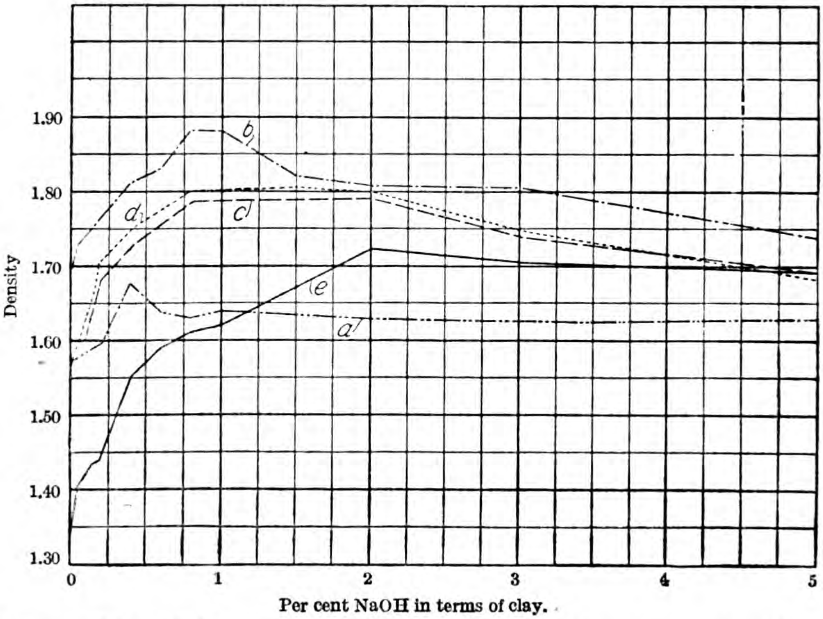


FIGURE 17.—Effect of NaOH on the dry density of different clays and mixtures. *a*, 50 per cent Georgia kaolin and 50 per cent flint; *b*, 50 per cent Tennessee ball clay and 50 per cent flint; *c*, 50 per cent Kentucky ball clay and 50 per cent grog; *d*, 50 per cent Kentucky ball clay and 50 per cent flint; *e*, Kentucky ball clay.

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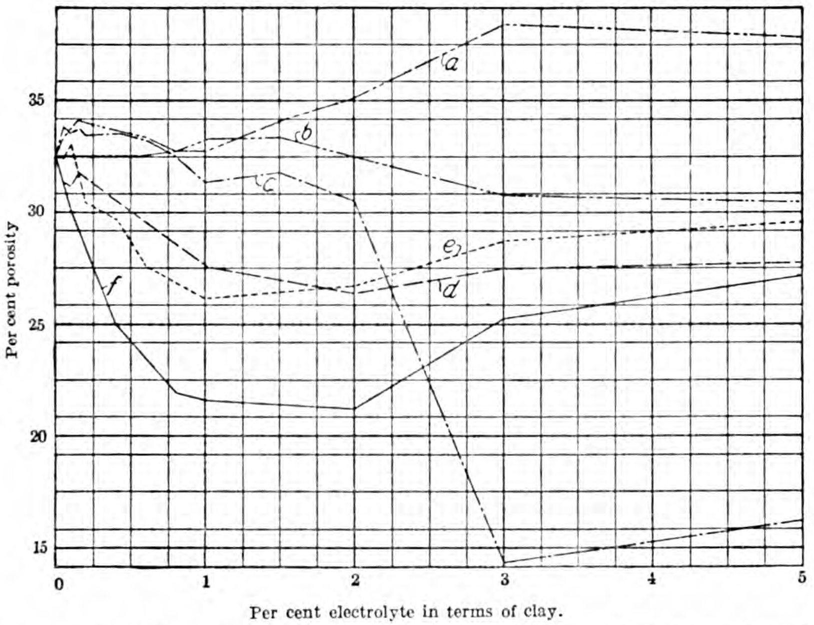

FIGURE 18.—Effect of electrolytes on the porosity of a mixture of 50 per cent Kentucky ball clay and 50 per cent flint. *a*, CaOH; *b*, tannic acid; *c*, H_2SO_4; *d*, Na_2CO_3; *e*, Na_2SiO_3; *f*, NaOH.

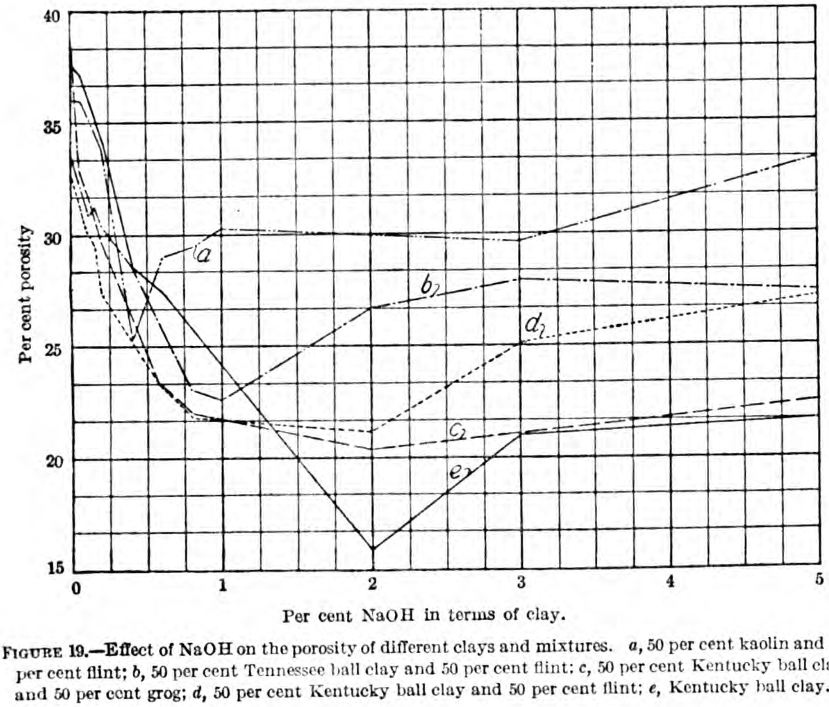

FIGURE 19.—Effect of NaOH on the porosity of different clays and mixtures. *a*, 50 per cent kaolin and 50 per cent flint; *b*, 50 per cent Tennessee ball clay and 50 per cent flint; *c*, 50 per cent Kentucky ball clay and 50 per cent grog; *d*, 50 per cent Kentucky ball clay and 50 per cent flint; *e*, Kentucky ball clay.

more is used it is increased. The body becomes more dense and the porosity becomes lower when caustic soda is used. Adding more than 1 per cent causes considerable scumming and surface vitrification.

Figure 21 shows the effect of the electrolytes on the strength of the mixtures fired to cone 8. Although the fluxing action of the alkalies improves the strength somewhat, there is a decided similarity between the effects on the fired and the raw strength, as is shown in figure 9. Here again the so-called "strong" electrolytes like NaOH are more effective than the weaker electrolytes like Na_2CO_3. The finer grained structure produced by deflocculation seems to be a factor influencing the fired strength as well as the dry strength of the bodies.

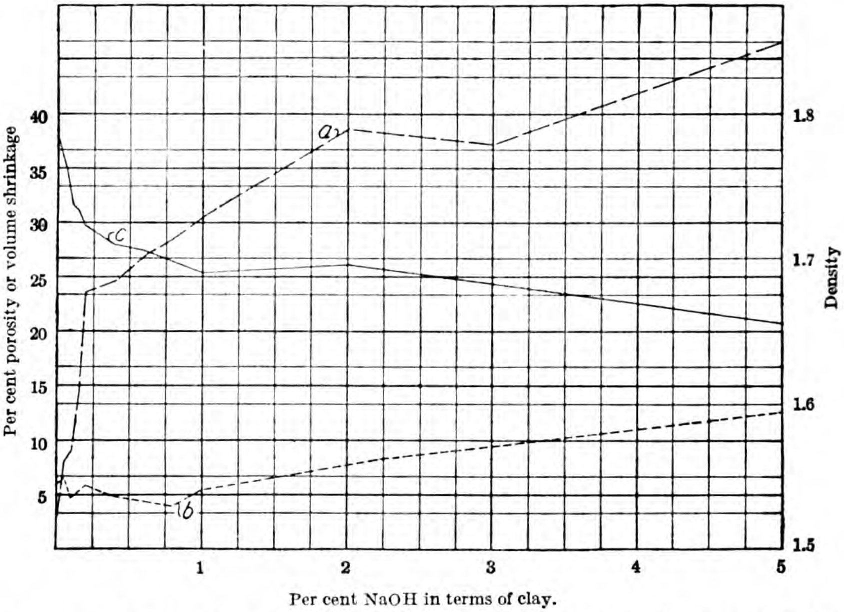

FIGURE 20.—Effect of NaOH on the burning properties of a mixture of 50 per cent Kentucky ball clay and 50 per cent flint fired to cone 01. *a*, Density; *b*, volume shrinkage; *c*, porosity.

Figure 22 shows the effect of NaOH on the behavior of Tennessee ball clay after firing at different temperatures. It is obvious that the greatest change produced by adding the NaOH was to decrease its burning shrinkage, this being reduced below that of English ball clay. NaOH also lowers the vitrification range slightly.

EFFECT OF WET GRINDING, SCREENING, ELECTROLYTES, AND DEXTRINE ON CLAYS OF LOW PLASTICITY AND STRENGTH.

DESCRIPTION OF TESTS.

Three clays were selected for this work, namely, (1) an Ohio stoneware clay, (2) a Maryland flint clay, and (3) an Ohio semiflint clay. These were crushed to 20-mesh size and mixed thoroughly by

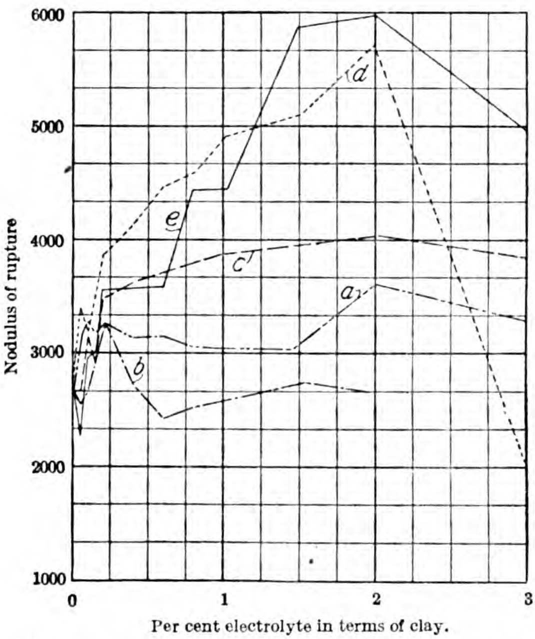

FIGURE 21.—Effect of electrolytes on the strength of a mixture of 50 per cent Kentucky ball clay and 50 per cent flint fired to cone 8. *a*, Tannic acid; *b*, H_2SO_4; *c*, Na_2CO_3; *d*, Na_2SiO_3; *e*, NaOH.

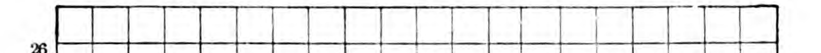

FIGURE 22.—Effect of NaOH on burning behavior of Tennessee ball clay and English ball clay. On shrinkage, a^1, Tennessee No. 3 ball clay; b^1, English ball clay; c^1, Tennessee No. 3 ball clay plus .7 per cent NaOH; on porosity, *a*, Tennessee No. 3 ball clay; *b*, Tennessee No. 3 ball clay plus .7 per cent NaOH; *c*, English clay.

shoveling. The total batch was then divided into 15-pound portions and treated as follows:

The 15-pound portions were ground wet in a small laboratory wet pan for 30, 60, and 120 minutes. The dimensions of the pan and mullers are as follows: Outside diameter of pan, $22\frac{1}{4}$ inches; inside diameter, 22 inches; diameter of mullers, $9\frac{3}{4}$ inches; thickness of mullers, $2\frac{3}{16}$ inches. The pan operated at 60 revolutions per minute. Distilled water was used in all experiments in order to eliminate the effect of the electrolytes present in city tap water, and thus to get more comparable results.

The clays were treated as follows:

1. Wet ground without the addition of electrolytes.
2. Wet ground with 1 per cent NaOH.
3. Wet ground with 1 per cent NaOH and the coarse material removed by screening the clay through a 150-mesh sieve.
4. Wet ground with 1 per cent NaOH, 1 per cent dextrine, and the coarse material removed by screening.

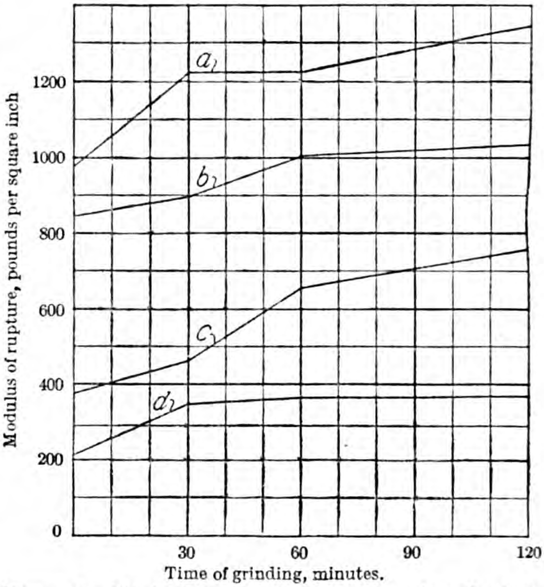

FIGURE 23.—Effect of treatment on the dry strength of an Ohio stoneware clay. *a*, Ground with 1 per cent NaOH and 1 per cent dextrine, and screened through 150-mesh; *b*, ground with 1 per cent NaOH and screened through 150-mesh; *c*, ground with 1 per cent NaOH; *d*, ground with pure distilled water.

Cross-breaking strengths were determined in the dry condition and after firing to cone 2. The water of plasticity, dry shrinkage, dry density, firing shrinkage, and porosity of the fired specimens were determined in the customary manner.

Elutriation tests were made also in order to compare the effect of these treatments on the fineness of the grain of the products. The elutriation tests were made as described [28], except that the clays were not deflocculated before the elutriation. The tests were made in this manner in order to compare the fineness of grain of those clays treated with 1 per cent NaOH with those not treated with electrolytes.

RESULTS OF TESTS.

EFFECTS OF TREATMENT ON STRENGTH.

The results of these treatments are shown in Table 10 and in figures 23, 24, and 25. With stoneware clay the dry strength was

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[28] Schurecht, H. G., Elutriation tests on American kaolins, Jour. Amer. Ceram, Soc., Vol, 3, 1920, pp. 355–357.

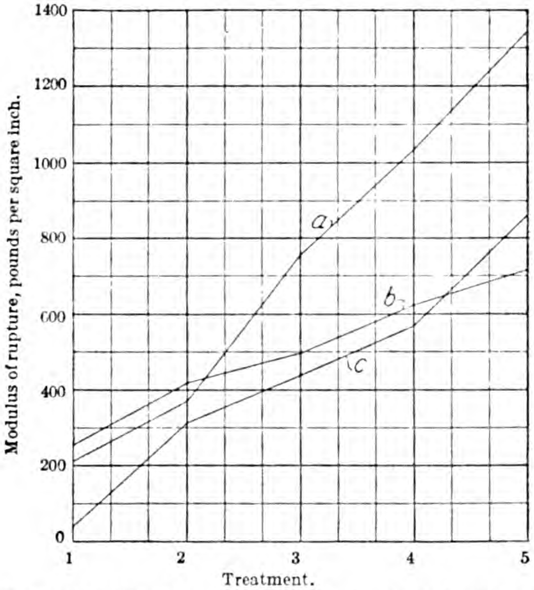

FIGURE 24.—Effect of treatment on dry strength. 1, Crushed to 20-mesh size, not ground wet; 2, wet ground two hours; 3, wet ground two hours with 1 per cent NaOH; 4, treatment as in 3 and screened through 150-mesh; 5, wet ground two hours with 1 per cent NaOH and 1 per cent dextrine and screened through 150-mesh; *a*, stoneware clay; *b*, semiflint clay; *c*, flint clay.

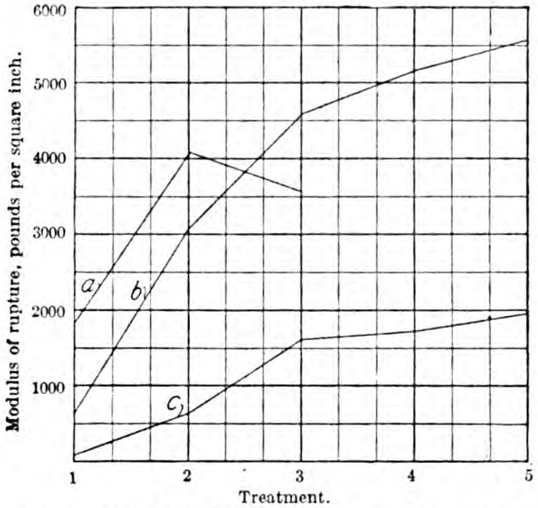

FIGURE 25.—Effect of treatment on strength after firing to cone 2. 1, Crushed to 20-mesh size, not ground wet; 2, wet ground two hours; 3, wet ground two hours with 1 per cent NaOH; 4, treated as in 3 and screened through 150-mesh; 5, wet ground two hours with 1 per cent NaOH and 1 per cent dextrine and screened through 150-mesh; *a*, stoneware clay; *b*, semiflint clay; *c*, flint clay.

increased 74.28 per cent by wet grinding. The same clay with no grinding, but with an addition of 1 per cent of caustic soda showed an increased strength of 79.22 per cent. By a combination of wet grinding and the addition of caustic soda an increase of 255.76 per cent was obtained.

TABLE 10.—*Effect of treatments on the raw and fired strengths of clays.*

Clays tested.	Time of grinding, minutes.	1		2		3		4	
		Nothing added.		Treated with 1 per cent NaOH.		Treated as in 2 and screened through a 150-mesh sieve.		Treated with 1 per cent NaOH and 1 per cent dextrine and screened through a 150-mesh sieve.	
		Dried at 110° C.	Fired at cone 2.	Dried at 110° C.	Fired at cone 2.	Dried at 110° C.	Fired at cone 2.	Dried at 110° C.	Fired at cone 2.
Stoneware	0	211.61	1,823.80	379.25	2,405.7	847.85	....	973.50	....
Do	30	346.68	3,274.90	458.31	3,318.8	895.89	....	1,221.20	....
Do	60	364.36	3,630.30	659.72	3,346.2	1,006.94	....	1,220.00	....
Do	120	368.81	4,080.70	752.83	3,554.4	1,034.39	....	1,345.00	....
Flint clay	0	35.31	65.20	....	....	....	....	....	....
Do	120	305.38	601.96	439.46	1,606.08	569.66	1,702.8	861.42	1,913.4
Semiflint	0	251.71	602.20	....	....	....	....	....	....
Do	120	416.20	3,045.20	499.46	4,591.5	620.52	5,171.1	713.61	5,593.3

The greatest percentage increase was noted with flint clay, which in the untreated condition has a modulus of rupture of only 35.31 pounds per square inch. By grinding two hours this figure was increased to 305.38 pounds per square inch. On the addition of 1 per cent caustic soda an additional increase to 439.46 pounds per square inch was obtained.

Screening the clays through a 150-mesh sieve and adding 1 per cent dextrine gave additional strength to all of the clays.

Some of the test bars containing caustic soda showed scumming after drying, especially in the batches that were not ground in a wet pan; those that were ground for two hours showed considerably less scumming. The addition of dextrine or the decrease of the content of NaOH to 0.5 to 0.7 per cent also corrected this fault.

The strength tests of the fired specimens showed a similar increase in strength due to wet grinding and the addition of caustic soda; only a small increase in strength was noted when dextrine was used, as dextrine, which is organic, is burned out of the clay, and the bonding effect is thereby destroyed.

EFFECT OF TREATMENT ON PLASTICITY.

The plasticity was increased in each of the clays by wet grinding, screening, and the addition of 1 per cent dextrine. The decrease in moldability through the addition of 1 per cent caustic soda was not as pronounced when 100 per cent clay was used as it was when 50 per cent flint was mixed with the clay. Judged by touch, those clays treated with soda seemed to be more plastic than those not so treated, although they were tougher and harder to mold. Wet grinding also increased the drying shrinkage, decreased the dry density, and increased the water of plasticity, whereas the firing shrinkage and porosity remained about the same when fired to cone 8 (see Table 11).

TABLE 11.—*Effect of treatments on the properties of clays.*

Clay tested.	Time of grinding.	1						2	3	4
		Nothing added.						Treated with 1 per cent NaOH.	Treated as in 2, screened through a 150-mesh sieve.	Treated with 1 per cent NaOH and 1 per cent dextrine; screened through a 150-mesh sieve.
		Drying shrinkage.	Dry density.	Water of plasticity.	Firing shrinkage, cone 8.	Porosity, fired at cone 8.	Surface factor.	Surface factor.	Surface factor.	Surface factor.
	Minutes.	*Per cent.*		*Per cent.*	*Per cent.*					
Stoneware..	0	13.55	1.98	18.50	18.47	0.351	7,352.40	5,705.66	....	....
Do......	30	14.07	1.86	22.86	18.45	0.245	....	12,061.75	....	....
Do......	60	15.93	1.84	22.87	18.52	0.800	9,385.96	13,102.32	....	....
Do......	120	15.79	1.85	23.40	18.50	0.610	9,385.96	13,384.64	....	....
Flint clay..	0	....	....	....	....	....	2,398.45	....	....	....
Do......	120	....	....	....	....	....	7,464.62	9,752.36	9,469.80	13,334.60
Semiflint...	0	....	....	....	....	....	5,643.36	....	....	....
Do......	120	....	....	....	....	....	9,951.20	10,604.93	13,930.06	14,003.98

RESULTS OF ELUTRIATION TESTS.

For the results of elutriation tests see Table 11. It is obvious that wet grinding increases the fineness of grain, as is shown by the increase in the surface factor of the clay after grinding. The addition of caustic soda to clay in grinding causes an additional increase in fineness owing to the dispersion of the aggregates of the colloidal clay. With stoneware clay wet grinding for two hours increased the surface factor 27.6 per cent, whereas wet grinding for two hours with 1 per cent NaOH increased the surface factor 81.9 per cent, indicating that soda was more effective than wet grinding in increasing the fineness of the grain. The flint and semiflint clays, on the other hand, are affected more by wet grinding than by the addition of NaOH, indicating that some clays respond more readily to wet grinding and others respond more readily to the treatment with soda. Clays of the colloidal type respond to soda more readily than clays of the crystalline type.

SUMMARY.

RATIOS OF SALT TO CLAY IN PURIFICATION.

Based upon the results of the investigation described in this paper the writer has drawn the following conclusions in those tests in which the water was relatively pure and in which the water content was greater than 50 per cent.

Though the chemical activity of the electrolyte on clay may be slightly less in the more concentrated solutions than in the dilute solutions, it is much more important in maintaining minimum viscosity in clay slips in which the clay and water contents vary to keep the ratio of electrolyte to clay constant than to keep constant the ratio of electrolyte to water.

When sodium hydroxide is added in small quantities to Georgia kaolin the decrease in viscosity is retarded up to a certain point, and then there is a sudden drop to minimum viscosity. Sodium carbonate or sodium silicate does not retard the increase in viscosity as does sodium hydroxide.

In agreement with Bleininger's work,[29] sodium hydroxide and sodium silicate proved to be much more effective reagents in lowering the viscosity than sodium carbonate.

The limits within which sodium hydroxide produces minimum viscosity are small, but the limits within which sodium silicate and sodium carbonate produce minimum viscosity are relatively large.

The viscosity data would indicate that 50 to 58 per cent more clay per unit quantity of slip can be treated when alkalies sufficient to produce minimum viscosity are added than when no alkalies are added. This point should be confirmed, however, by large-scale tests under clay-washing practice.

USE OF SULPHURIC ACID IN SEDIMENTATION.

The data indicate that with Florida and North Carolina kaolins the viscosity is increased when the slip is neutralized with sulphuric acid equivalent to the sodium hydroxide first added. To reduce this effect an amount of sulphuric acid less than the equivalent of sodium hydroxide should be added, the amount varying with different clays.

With Florida and Georgia kaolins the sedimentation was much slower after the slips had been treated with sodium hydroxide and sulphuric acid than it was before treatment.

In some cases black discoloration on the dry kaolin is caused by adding an excess of sulphuric acid. The proper amount necessary to overcome this trouble must be determined for each clay. It appears

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[29] Bleininger, A. V. Use of sodium salts in the purification of clays and in the casting process: Bureau of Standards Tech. Paper 51, 1915, p. 39.

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that the necessary amount is less than the equivalent amount of sodium hydroxide.

The deflocculated kaolin could not be filtered successfully as the fine particles either passed through or clogged the filter. Partly neutralizing the alkalinity of the kaolin by adding sulphuric acid permits ready filtration.

The rate of disintegration of the deflocculated kaolin in water is much slower than that of the untreated kaolin.

Care should be taken to add the proper amount of acid to alkalies in the kaolin slip, because any variation of acid causes the kaolin to act differently toward subsequent alkali treatment. Those slips that have been treated with larger additions of sulphuric acid require more alkalies to produce the same degree of dispersion upon redeflocculation.

ELECTROLYTES AND PLASTIC BODIES.

The dry strength may be increased by adding the following electrolytes to the bodies in the plastic state. In the order of their effectiveness these electrolytes are as follows: (1) Sodium hydroxide, (2) sodium silicate, (3) sodium carbonate, (4) tannic acid, and (5) calcium hydroxide.

When caustic soda was employed, the strength of some of the treated clays was increased to 400 per cent of that of the untreated clays. Sulphuric acid in small percentages lowers the strength of Kentucky ball clay. When more than 2 per cent calcium hydroxide is used the strength of Kentucky ball clay is decreased.

With 0.8 to 2.5 per cent caustic soda the bodies containing 50 clay and 50 flint become difficult to mold and will not retain their shape unless the mass contains a low percentage of water. This effect is also noticeable to a smaller degree when sodium silicate, sodium carbonate, or more than 2 per cent of sulphuric acid are employed, but it is less perceptible when calcium hydroxide, tannic acid, or a body containing 100 per cent clay is used. Less than 2 per cent sulphuric acid produces better moldable bodies than the untreated bodies.

With the two ball clays the alkalies lower the percentage water of plasticity. The acids at first increase and then with an excess decrease the water necessary to work the bodies. Calcium hydroxide increases the water of plasticity.

When 1 to 2 per cent alkalies are added the volume shrinkage is lowered in all 50 clay and 50 flint mixtures except with Georgia kaolin, in which the shrinkage is increased. With Kentucky ball clay alone the shrinkage is increased upon the addition of sodium hydroxide. Sulphuric acid in small percentages increases the shrinkage and in larger percentages decreases the shrinkage. Tannic acid and calcium hydroxide increase the shrinkage.

Alkalies and acids make the clays and mixtures more dense in the dry state. Additions of calcium hydroxide make the bodies more dense up to 1 per cent, beyond which the reverse is true.

The porosity is also decreased by adding alkalies. Acids in small percentages make the bodies more porous, but in larger quantities lower the porosity. Calcium hydroxide makes the body more open.

Examination with the microscope showed that the clays treated with NaOH have the fine grains characteristic of deflocculated clays. The increase in mechanical strength may be largely due to the fact that the finer grains would pack more closely and hence make a denser body.

The effect of acids is the reverse of the effect of alkalies. Therefore it appears that the changes produced are functions of the alkalinity or acidity of the bodies.

In all cases the so-called "strong" electrolytes, those having a high degree of ionization like NaOH, were much more effective than the "weaker" electrolytes like $Na_2 CO_3$.

The shrinkage on firing to cone 01 is lowered when small percentages of caustic soda are added, and is increased when larger quantities are used. The fired porosity becomes less and the density becomes greater upon the addition of sodium hydroxide.

It requires five times as much NaOH in terms of clay to produce maximum dry strength in a plastic clay containing about 25 per cent water as is necessary to produce the minimum viscosity in a clay slip containing over 50 per cent water. Evidently the decreased ionization of electrolyte caused by the evaporation of water in drying decreases the chemical activity of the electrolyte when added to plastic clay.

The strength after being fired to cone 8 appears to be increased by adding the following electrolytes to the bodies in the plastic state, named in order of effectiveness: (1) Sodium hydroxide, (2) sodium silicate, (3) sodium carbonate, and (4) tannic acid. Although the fluxing action of the alkalies improves the strength, the data for fired and for raw strength show a decided similarity. The so-called "strong" electrolytes are more effective than the weaker ones; hence, it seems that the finer grains produced by deflocculation influence the fired strength as well as the dry strength of the bodies.

Although the foregoing results applied to most of the clays, exceptions appeared in later work.[30] For example, the addition of NaOH seems to have the opposite effects on English ball clay (Dorset clay) and Mississippi ball clay in graphite crucible bodies, perhaps on account of a difference in the initial alkalinity or acidity of the clays.

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[30] Schurecht, H. G. The effect of electrolytes on bodies containing graphite: Jour. Amer. Ceram. Soc., vol. 2, 1919, pp. 443–450.

EFFECT OF TREATMENTS ON CLAYS OF LOW PLASTICITY AND STRENGTH.

The following summary of the effect of different treatments on clays of low plasticity and strength is based upon the results of the foregoing investigation.

The dry strength of the clay is increased 76.2 to 675 per cent by wet grinding in a wet pan for two hours.

An additional increase in dry strength of 19.1 to 78.3 per cent is obtained by adding 1 per cent NaOH to the clay in grinding.

Removal of the coarse material by screening the clay through a 150-mesh sieve increases the strength an additional 24 to 35.5 per cent. The addition of 1 per cent dextrine causes an increase in strength of 16.1 to 52.6 per cent, depending on the clay used.

A combination of the above treatments causes an increase in dry strength of 188 to 2,050 per cent.

The plasticity of all clays is increased by wet grinding, screening, and the addition of 1 per cent dextrine.

The addition of 1 per cent NaOH causes the clay to become tougher in the plastic condition and somewhat more difficult to mold.

Scumming was noticed in some tests in which soda had been used and no wet grinding given the clay. Scumming may be overcome by the use of 1 per cent dextrine with the soda or by using a smaller percentage of soda, 0.5 to 0.7 per cent.

The drying shrinkage is increased, the density decreased, and the water of plasticity increased by wet grinding.

The fineness of grain of the clays is increased by wet grinding and an additional increase is obtained by adding 1 per cent of NaOH.

The strength of the clays after firing to cone 2 was increased 127 to 1,700 per cent by the treatments described above.

NECESSARY PRECAUTIONS AND SPECIAL TREATMENTS.

An outline of some precautions necessary in the purification of clays and methods for changing their properties by special treatments in their preparation is given below. Some of the treatments suggested are too costly for the cheaper grades of ware, but might be used for the finer grades.

To maintain maximum dispersion in clay slips whose clay and water contents vary, the alkalies should be added in terms of clay rather than in terms of water.

To prevent the plasticity of chemically treated kaolins from becoming greater than that of the original kaolin, add slightly less than an equivalent amount of H_2SO_4 to the slip in neutralizing the alkalies in the sedimentation of clays. The amount will vary with different clays and should be checked by viscosity measurements of the clay slip. The viscosity should be the same as that of the original slip.

To prevent black discolorations on kaolin after drying: As the black discoloration is often caused by adding an excess of sulphuric acid, adding less than an equivalent amount of sulphuric acid to neutralize the soda generally prevents scumming.

To prevent kaolin from passing through the filter press, add a flocculating agent like sulphuric acid.

To increase the dry strength, add binders, as described below:

Treatment.	Possible increase, per cent.
Add 2.0–3.0 per cent tannic acid	33.0–43.0
Add 1.0 per cent dextrine	16.1–52.6
Add .25–2.0 per cent Na_2CO_3	25.0–108.0
Screen through a 150-mesh sieve	24.0–123.5
Add 0.25–2.0 per cent Na_2SiO_3	40.0–170.0
Add 0.25–1.0 per cent NaOH	75.0–250.0
Grind in a wet pan 2 hours	76.2–675.0
Grind in a wet pan with 1 per cent NaOH and 1 per cent dextrine and screen through a 150-mesh sieve	188.0–2,050.0

To decrease the water of plasticity, add electrolytes as described below:

Treatment.	Possible decrease, per cent.
Add 0.5–1.0 per cent Na_2CO_3	4.0–14.0
Add 0.5–1.0 per cent Na_2SiO_3	10.0–25.0
Add 0.25–.8 per cent NaOH	16.0–30.0

To increase the dry density, use the treatment indicated:

Treatment.	Possible increase, per cent.
Add 1.0 per cent $Ca(OH)_2$	2.5
Add 2.0–3.0 per cent tannic acid	2.5–3.2
Add 0.25–1.0 per cent Na_2CO_3	4.0–9.0
Add 0.25–1.5 per cent Na_2SiO_3	5.1–11.5
Add 0.25–1.0 per cent NaOH	9.0–15.0
Add 2.0–3.0 per cent H_2SO_4	3.0–17.0

To decrease the dry density:

Treatment.	Possible decrease, per cent.
Add 3.0–4.0 per cent $Ca(OH)_2$	1.2–4.4
Grind in a wet pan for 2 hours	6.5

To increase the fired strength, treat as indicated below:

Treatment.	Possible increase, per cent.
Add 0.25–2.0 per cent tannic acid	20.0–40.0
Add 0.25–2.0 per cent Na_2CO_3	40.0–50.0
Add 0.25–1.2 per cent Na_2SiO_3	50.0–110.0
Add 0.25–1.5 per cent NaOH	30.0–120.0
Screen through a 150-mesh sieve	5.9–126.0

To increase the water of plasticity, grind in a wet pan 2 hours. Possible increase, 26.5 per cent.

To decrease the drying shrinkage, add reagent as shown below:

Treatment.	Possible decrease of volume shrinkage, per cent.
Add 0.8 per cent $NaOH$	10.0
Add 0.5–1.0 per cent Na_2SiO_3	5.0–14.0

To increase the drying shrinkage, treat as shown below:

Treatment.	Possible increase of volume shrinkage, per cent.
Add 2.0–5.0 per cent tannic acid	3.0–10.0
Add 1.5–2.0 per cent Na_2CO_3	10.0–14.0
Grind in a wet pan for 2 hours	16.6
Add 1.0–2.0 per cent $Ca(OH)_2$	10.0–18.0
Grind in a wet pan for 2 hours	123.5–823.8
Grind in a wet pan with 1 per cent $NaOH$ and 1 per cent dextrine for 2 hours and screen through a 150-mesh sieve	775.0–1,320.0

To decrease the fired strength, add .6 per cent H_2SO_4. Possible decrease, 4.0 per cent.

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